STUDIES ON THE ADSORPTIVE SEPARATION TECHNIQUES WITH REFERENCE TO SEPARATION OF ISOMERIC MIXTURES OF GLUCOSE AND FRUCTOSE

A Thesis Submitted

In Partial fulfillment of the requirements

for the degree of

Master Of Technology

By

CHAVAN ABHIJIT R.

To the

Department of Chemical Engineering

Indian Institute of Technology , Kanpur

June 1996

CERTIFICATE

It is certified that the work contained in the thesis entitled " Studies on the adsorptive separation techniques with reference to separation of isomeric mixtures of glucose and fructose," has been carried out by Mr. Chavan Abhijit R. under my supervision and this has not been submitted elsewhere for a degree.

Dr. J.K. Gehlawat
Professor
Department of Chemical Engineering ,
Indian Institute of technology ,Kanpur.

7th June 1996

Acknowledgements

I express my deep sense of gratitude to my thesis supervisor Prof. J. K. Gehlawat for his constant help and encouragement throughout this work. He has shown a lot of patience and kindness to me. He was always ready with spontaneous solutions to whatever problems I got.

My sincere thanks are to Prof. D. P.Rao for his kind help to me. He taught me how to explore the things and I really miss him because of his sudden two year visit to United States since September , 1995. Partial financial support from M/s Engineers India Ltd. is gratefully acknowledged.

My sincere thanks are to my labmate Dr. S. Kumar who was very helpful throughout my work . I learned a lot of things from him. I am also thankful to Pavitra Sandilya for his kind help to me. The patience he has shown is really memorable especially when I ask him very simple questions.

My sincere thanks are to my friends Sanjay Singh , Upadhye, Prabhat, Rajneesh, Verma, Rathi, Anil Kumar, Murthy, Bhargava Ram, Kohli, Majumdar, Shyamal,Chakki, Prasad, Deshpande, Sanjay Shinde, Ghosh, Doma, Chander, Sajid and many others who not only helped me but made my stay at I.I.T./K pleasant and memorable .

I am also thankful to Mr. Virdi of Workshop, R.D.Singh, Nagendra, Badlu, Ramchandraji who were very cooperative and always ready to extend their helping hand.

Of course the love and blessings of my beloved parents and siblings have been always with me.

Chavan Abhijit R.

Contents

Abstract

Of recent, there has been a growing interest in the study of supplementary sweeteners. High fructose syrup (H.F.S.) which may be produced from isomerization of glucose or from invert sugar is one of such alternative. The basic raw materials for this product are starch and cane-juice. Starch can be produced from cheap sources like maize, jowar, broken rice etc. The hydrolysis of starch produces glucose which may be isomerized to produce equilibrium mixtures of glucose and fructose . The technological developments for the enrichment process applied to the commercial production of H.F.S. are of recent origin. Adsorptive separation technique using suitable ion exchange resins have been found to be commercially attractive for the separation of glucose and fructose from their aqueous mixtures .

In this study, indigenous resins in Ca^{++} form were used for the separation of aqueous solution of glucose and fructose. High performance liquid chromatograph (H.P.L.C.) was used to analyze the product composition. The effects of flowrate, feed concentration and bed height have been studied.

The breakthrough curves of adsorption of glucose and fructose on ion exchange resins were obtained. The effects of temperature and feed concentration on breakthrough curve were studied. The equilibrium constants for glucose and fructose were determined for the ultimate design of simulated moving bed operation.

In practice a moving bed adsorber is preferred for the separation of glucose and fructose. But it is difficult to circulate the solid adsorbents in the apparatus. Hence a simulated moving bed adsorber is to be preferred for industrial applications . An attempt has been made to model a simulated moving bed adsorber. The equations

have been solved using the Gauss-Jordan technique. A close agreement between the experimental and theoretical concentration profiles has been observed. The effects of operating parameters like switch time, column length , flowrates of the extract , raffinate , feed and the desorbent have been studied for optimal separations.

List of figures

List of tables

Chapter 1

Introduction

Adsorptive separation processes are of great industrial significance. They are used to separate isomeric compounds which are difficult to separate by the conventional methods like distillation,crystallization etc. The basic principle of separation relates to the preferential adsorption of one component (or a family of similar components) from a mixed feed. The selectivity of the adsorbent is a key factor in determining the viability of adsorption separation processes. This selectivity depends upon the differences in sorption equilibrium or less commonly on a difference in sorption kinetics.

Adsorbents are generally used to remove trace components from gases and liquids. The use of charcoal for water treatment and bone char for removal of coloring matter from sugar solutions in sugar industry are some of the familiar but simple examples of domestic and industrial uses of adsorption. More complex techniques like chromatographic separation are also based on the difference in the affinities of solutes towards an adsorbent. Paper chromatography, thin layer chromatography (TLC), column chromatography including gas and liquid chromatography are used for the chemical analysis. High performance liquid chromatography (HPLC) and gas chromatography are fast becoming indispensable for analytical work. The application of these techniques on industrial scale is being promoted. For example, the largest application of adsorptive separation technique on industrial scale are for the

separation of isomeric mixtures of xylenes (ortho and para) and glucose and fructose content from its aqueous mixtures with glucose on industrial scale.

Recently, high fructose syrups (H.F.S.) have emerged as cheaper alternative sweeteners. They have replaced the traditional sucrose (cane ,beet sugar) by more than 50 % in advanced countries like the united states of america. H.F.S. are produced conventionally from starch (maize,corn). Gehlawat (1,2) has discussed the relevance of commercial production of H.F.S. in India. A distinct possibility of producing H.F.S. from sugarcane juice has been highlighted by Gehlawat and Gehlawat (2) and Kumar and Gehlawat (3). High fructose syrups are manufactured by isomerization of high purity (+98 DE) starch hydrolyzates using immolized glucose isomerase as a biocatalyst. A mixture containing about 42 percent fructose and 58 percent glucose is obtained. Commercially acceptable syrups must contain minimum 55 to 60 percent fructose in order to meet the sweetness index as well as to reduce the tendency for glucose to crystallize from such mixture on storage. This is achieved by enrichment of fructose content in the mixture of glucose and fructose by the adsorptive chromatographic technique.

Schoenrock et.al. (4) have explored the possibility of producing H.F.S. from sugar through its cationic inversion. Studies by Doelle and Doelle (5) have also described the formation of fructose from sugarcane syrup and molasses. Kumar and Gehlawat (3) have also discussed production of H.F.S. from cane juice.Thus, the production of H.F.S. from sucrose (canejuice) is a distinct commercial possibility.

Invert sugar finds application in confectionery, beverages, bakery, food and pharmaceutical formulations. The conventional method of producing invert sugar using mineral acids suffers from low conversion efficiency (65 to 70 percent), high ash content and undesirable end products (7 to 8 percent) (2). Moreover, the invert sugar thus obtained is dark in colour. In view of these drawbacks (of the conventional

process), attempts have been made to develop alternate methods to develop to produce invert sugar under milder conditions. Enzymatic hydrolysis of sucrose with invertase has been recommended by Monsoon and Combes (6) and Mansfield et.al. (7). Recently , the use of an immobilized invertase as a catalyst in a fixed bed reactor is claimed to produce low cost invert sugar syrup of high purity (8).

Inversion of sucrose may be carried out using cationic resins. Strong cationic resins behave as catalysts in liquid media. They possess excellent catalytic properties comparable to strong mineral acids. By choosing a cation exchange resin of proper acidity and porosity, any degree of sucrose inversion could be achieved without the introduction of any electrolyte into the syrup (9,10,11). Thus, inversion of sucrose using cation exchange resins may work out to be a cheaper commercial process for invert sugar under Indian conditions (2). Canejuice is the principle source of sucrose. The raw canejuice may be clarified by membrane techniques like ultrafiltration to eliminate colloidal organic impurities and electrodialysis to remove inorganic salts (12-16). The clarified canejuice thus obtained may be inverted using cation exchange resins as discussed by Sinha and Gehlawat (16) and Gehlawat and Gehlawat (2) and Kumar and Gehlawat (3). Fig 1.1 depicts chemistry for the formation of fructose from two alternate routes as also the method of enrichment of fructose.

In this work, an attempt has been made to study and model the process of separating glucose and fructose from their aqueous mixtures using adsorptive technique. This process is of great industrial importance for the production of high fructose syrups.

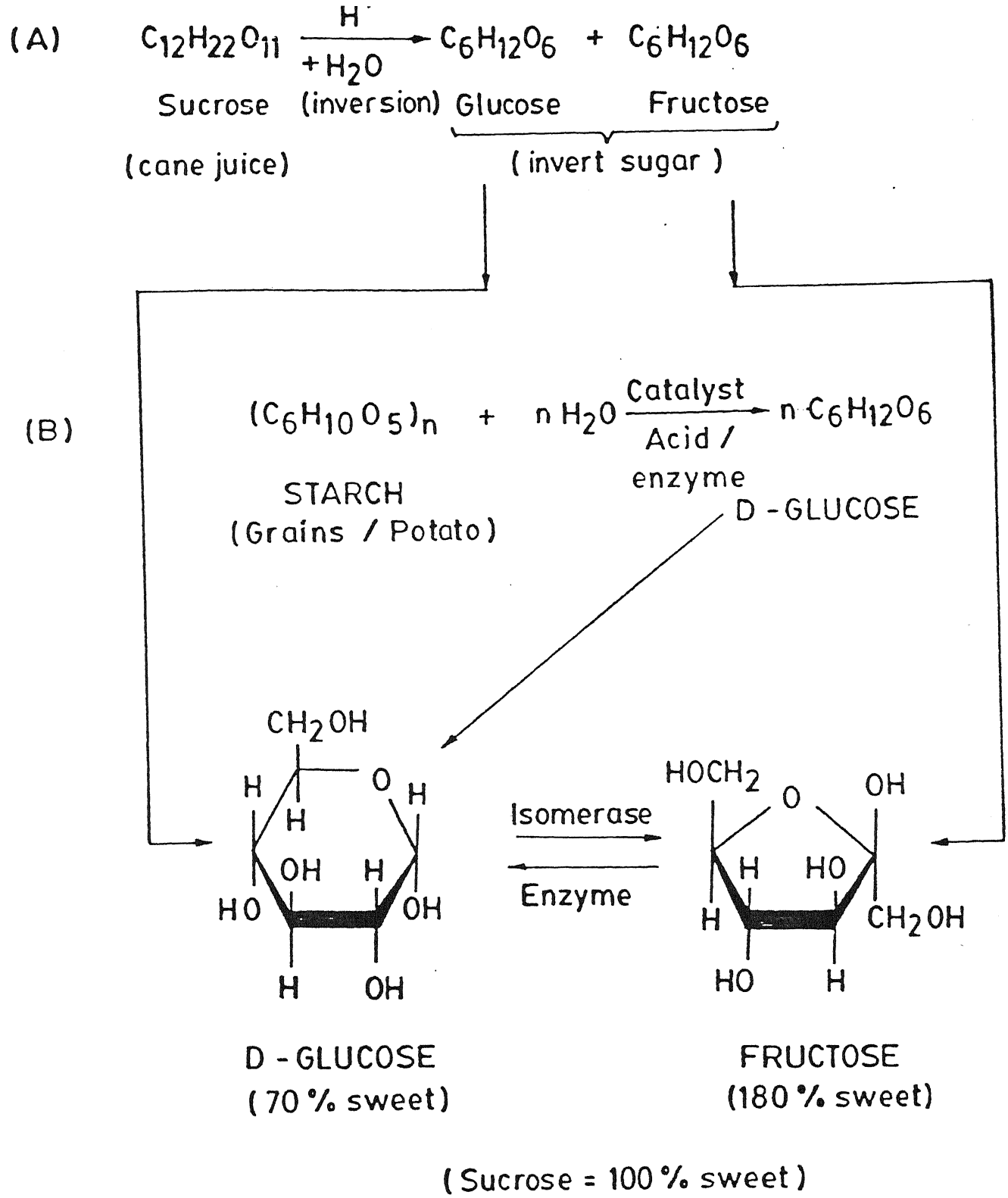


Fig. 1.1 : Chemistry of fructose production

Chapter 2

Literature Survey

2.1 High fructose syrup from two sources :

Two alternative processes may be used to obtain the mixtures of glucose and fructose as shown in fig. 1.1. The conventional method uses starch as a starting material. In this process, starch is hydrolyzed to glucose which in turn is isomerized into fructose using an immobilized enzyme as a catalyst. Apparently, this process is far more complex than the inversion of sucrose to obtain an equimolar mixture of glucose and fructose. High fructose syrups are obtained by an enrichment of the fructose content in the mixtures containing glucose and fructose which may be produced by either of these two alternate schemes.

2.2 Separation of glucose and fructose from their aqueous mixtures :

It is extremely difficult to separate glucose from fructose from their aqueous mixtures. Low temperature crystallization has been attempted (17,18,19). However, low temperature crystallization is not a practical proposition.

Glucose and fructose are known to have different affinities towards different adsorbents. This property could be successfully exploited for the separation of glucose and fructose from their aqueous solutions. Suitable adsorbents have been developed indigenously for this purpose (20).

The adsorptive separation technique is far more energy efficient than other methods like distillation, crystallization. It is because the separation is achieved

essentially at atmospheric pressure and at low temperature. Further, very favorable equilibrium phase relations can be developed for specific separations. Also it is possible to synthesize adsorbents which are much more selective in their affinity for various substances are, any known solvents. In this instance, suitable adsorbents have been developed indigenously.

2.3 Modes of operation of adsorption processes:

Essentially these can be classified as batch, semicontinuous and continuous processes. the details are given briefly in the following. The terms used are general. The feed is assumed to be a binary mixture of A and B, dissolved in a desorbent (solvent) D. the component A is more preferentially adsorbed as compared to component B. Further, the desorbent is a material capable of reversibly displacing components A and B from the solid while becoming adsorbed itself.

2.3.1 The fixed bed operation :

The arrangement of the fixed bed operation is shown in fig. 2.1. This is simplest form of operation. Alternate streams of feed (A+B) and desorbent D are fed to the column equipped with a fixed bed of the pertinent adsorbent. As the feed travels through the column, bond formation takes place as shown in fig. 2.1. Alternate streams of raffinate (rich in component B) and extract (rich in component A) can be obtained from the bottom of the column. The process is repeated to obtain intermittent supplies of raffinate and extract which may be suitably processed further. The most undesirable thing about this operation is its discontinuity. Controlling is a major problem for such operations, especially when performed on large scale basis. Mathematical modelling is also difficult due to discontinuity of the operation.

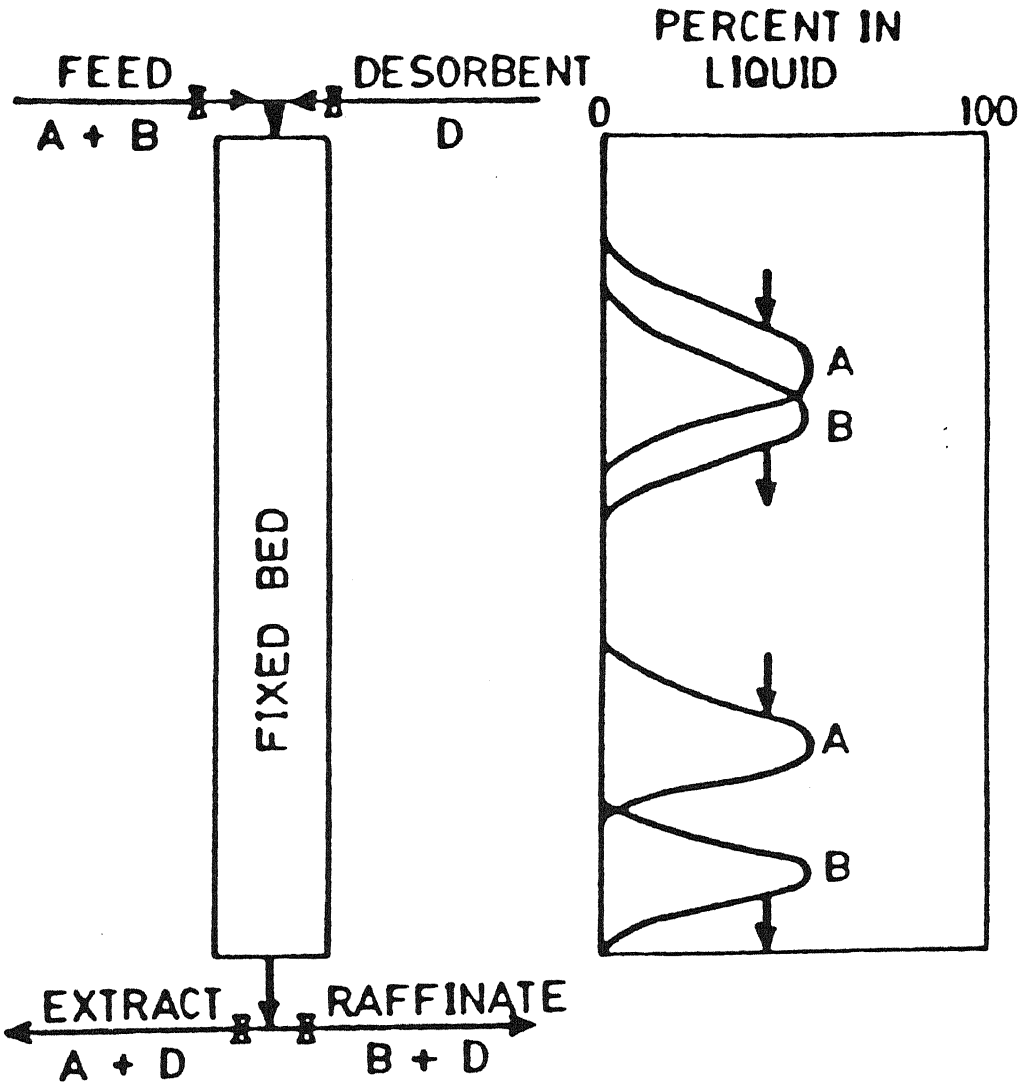


Fig. 2.1 : The fixed bed operation

2.3.2 The moving bed operation :

This is a continuous process. The details are shown in fig. 2.2. As shown in the figure, the solid phase is conveyed continuously down through the bed and recycled to the top of the adsorber. The bed is hypothetically divided into four zones for the purpose of analysis. Feed (A+B) is introduced at an intermediate stage between zones 1 and 2 as shown. Desorbent (D) is introduced near bottom between zones 3 and 4. Raffinate stream (B+D) is withdrawn from top and extract stream (A+D) from a point between zones 2 and 3. Liquid streams flows upwards through the column counter-current to the solid phase. Component A is adsorbed more firmly than component B. Zonewise the observable changes in the system are described in the following.

In zone 1, the entering solid contains only B and D as adsorbed components. As the solids descend, component A is adsorbed on the solid phase from the liquid stream. The component A is assumed to be completely removed from the rising stream and by the time it reaches the top, the liquid stream essentially containes only components B and D. This stream is taken out from the top as raffinate.

Zone 2 is primarily an enrichment zone. It is assumed that the component B is completely desorbed from the solids in this zone. the solids entering this zone contains both A and B as adsorbed components, since it has just been in contact with the fresh feed. Liquid entering the bottom of this zone contains only A and D. As the solids descend, the adsorbed component B is gradually desorbed from the solids by the rising liquid stream of A plus D. Because component A is more firmly adsorbed than B under certain conditions it is possible to achieve complete removal of component B from the solids without simultaneously removing adsorbed component A.

Zone 3 is a desorption zone which serves to remove adsorbed component A completely from the solids. The solids entering this zone carry A and D as adsorbed components. Liquid entering the bottom contains only the desorbent D. As the solids

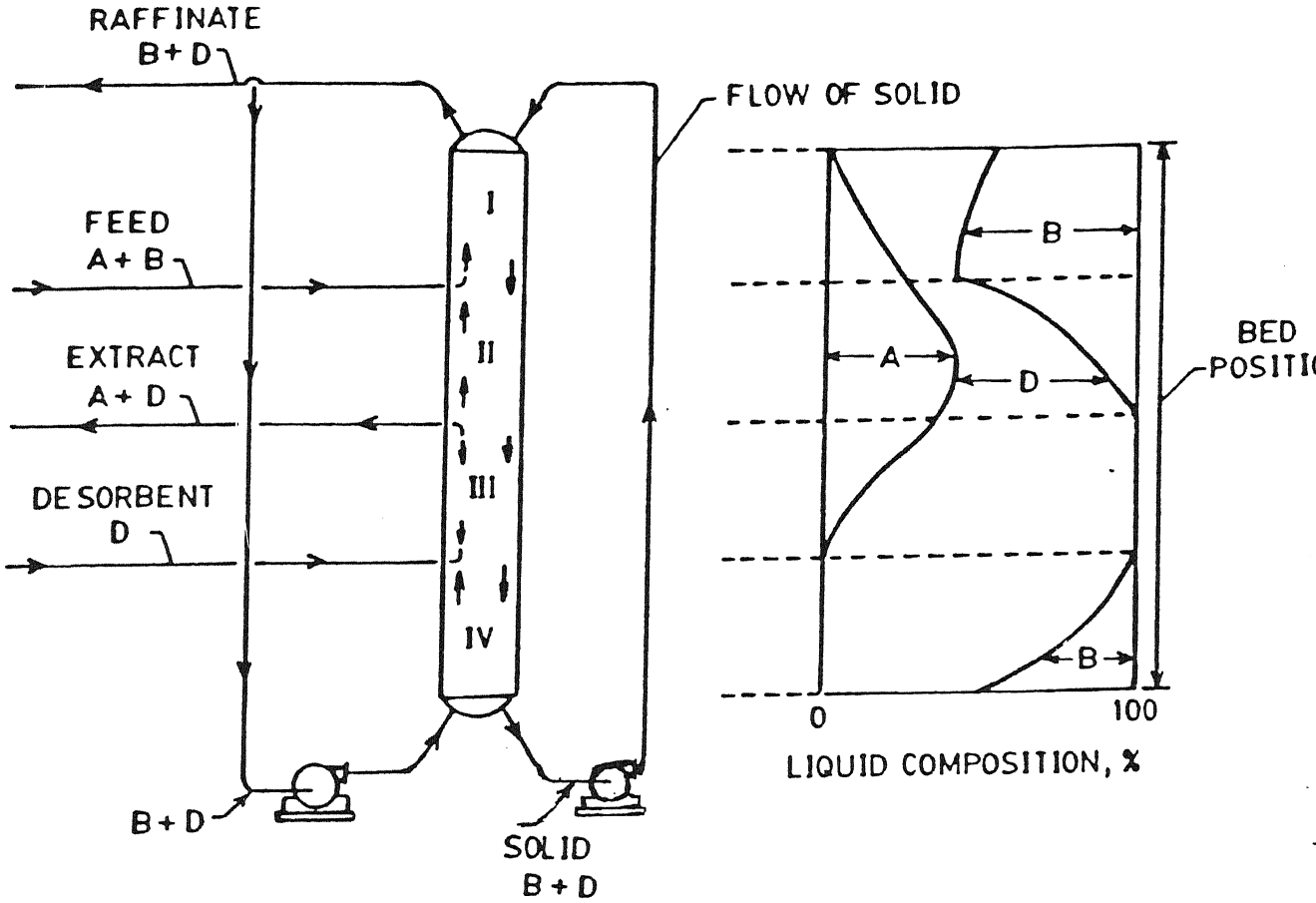


Fig. 2.2 : The moving bed operation

descend, adsorbed component A is gradually desorbed by D and is removed from the solids. A stream containing A+D is withdrawn as extract from the top of zone 3 as shown in figure.

In zone 4, a portion of adsorbed component D is removed from the solids entering this zone by the rising stream of liquid containing components B and desorbent D. The quantity of D thus removed from the solids then rises into zones 3 where it functions effectively as a desorbent. A typical concentration profile of various components (A and B) is also shown in fig. It is evident that an optimum system design of a moving bed could provide high operational efficiency. It is also evident that a continuous counter-current moving bed design is far more efficient than a fixed bed operation where the adsorbent bed is not fully utilized in a once-through operation.

The moving bed operation, though attractive, is not feasible industrially. To maintain a near plug-flow behaviour of both the phases is a major problem. The most difficult part is the pumping of solid adsorbents. Further there is an ample scope for the liquid to channel as the bed is prone to show up cracks during the operation. Other important problem is the mechanical vulnerability of the adsorbent which may not withstand the continuous movement.

2.3.3 The simulated moving bed operation :

The simulated moving bed process is developed with the idea that the effect of movement of the solids past fixed positions of liquid feed and withdrawl can be achieved by a sequential movement of the positions of the feed and withdrawl past the fixed bed (21). Such an arrangement is shown in fig 2.3. A shift in the positions of the inlet/outlet ports in the direction of flow of liquid simulates the movement of the bed in the opposite direction. This is achieved by providing a large number of openings

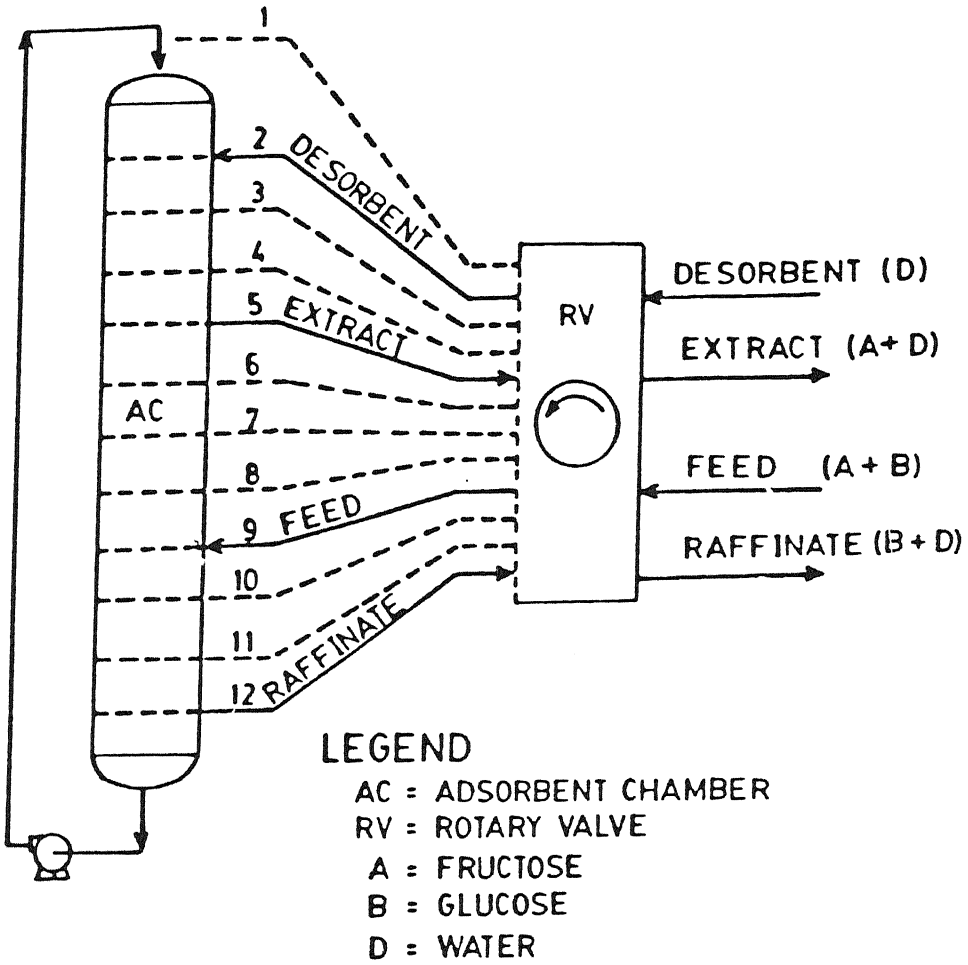


Fig. 2.3 : The simulated moving bed operation

along the length of the column. The change in the inflow/outflow streams to the column in the desired direction is achieved with the help of a rotary valve. Each of the access line in the column is attached to the distributor within the bed and terminates outside at a rotary valve. The rotary valve works on the principle same as a multiport-stop cock. It is able to direct all the flows simultaneously in different directions as per need. The effect of moving bed is obtained by simply rotating the valve in a programmed manner. This process is not truly continuous but, the greater the number of the access lines, the greater is the extent of continuous operation. Efforts are in progress to develop a truly continuous process as evidenced by the successful use of continuous annular chromatography (CAC) (22). But its commercial success is yet to be explored.

2.4 Modeling of adsorption processes :

General modeling aspects of different kinds of adsorption processes have been discussed in the following texts by Amundson et.al. (23,24), Rodrigues and Tondeur (25) and Ruthven (26).

Fixed bed operation is the simplest one and yet it gives complex material balance equations. The analytical solutions are difficult to obtain. Approximate solutions can be obtained only under highly simplified assumptions. Some of the classic models are the Thomas' model (27) and the Rosen's model (28). the most undesirable thing about the fixed bed operation is its discontinuity. Controlling is a major problem for such operations, especially when performed on large scale. Mathematical modeling is also difficult due to this undesirable property of discontinuity. Several mathematical models have been developed for the continuous counter-current moving bed operations. Kasten and Amundson (29) modelled an isothermal counter-current moving bed system having one dimensional flow of porous,

spherical particles, one dimensional fluid flow and a single component fluid phase entering at the bottom of the column. For fluid-solid equilibrium and a linear isotherm, an analytical solution was obtained. An equilibrium one dimensional flow model differing from Kasten and Amundson is that the feed is introduced at a side port and external mass transfer to the solid particles is rate controlling. This model proposed by Yoon and Kunii (30) yielded analytical solutions.

A theoretical model for simulation of semicontinuous chromatographic refiner (SCCR 4) is reported by Ching (31). The mathematical model proposed by Ching (31) is based on the equilibrium staged method. The design parameters N, HETP, K_d were calculated based on chromatographic responses of the component on the adsorption bed. Adsorption isotherms were assumed to be linear and non-interactive. Ching and Ruthven (32) presented a model for calculation of concentration profiles in SCCR 4, assuming that it could be expressed as continuous counter-current adsorber as shown in fig. 2.4. Plug flow of solids and dispersed plug flow of liquids were assumed. Ching and Ruthven (33) reported the transient behaviour of SCCR 4. They presented a theoretical approach for evaluation of system dynamics. As iterative process of calculating concentration profiles was time consuming. Exprimentally measured feed point concentrations were used as initial guess for the post feed concentration profile calculations. Lee et.al. (34) have proposed a theoretical model and solved it using orthogonal collocation technique. Hashimoto et. al. (35) have presented a mathematical model to solve the SMB(simulated moving bed) with and without assuming it to be equivalent to the continuous counter-current adsorber. They have observed that pseudo steady-state concentration profiles predicted by both the models are in agreement with the experimental results.

Hidajat et.al. (36) predicted both transient and steady state profiles numerically using Gear's algorithm. To attain the steady state fast the system was preloaded with

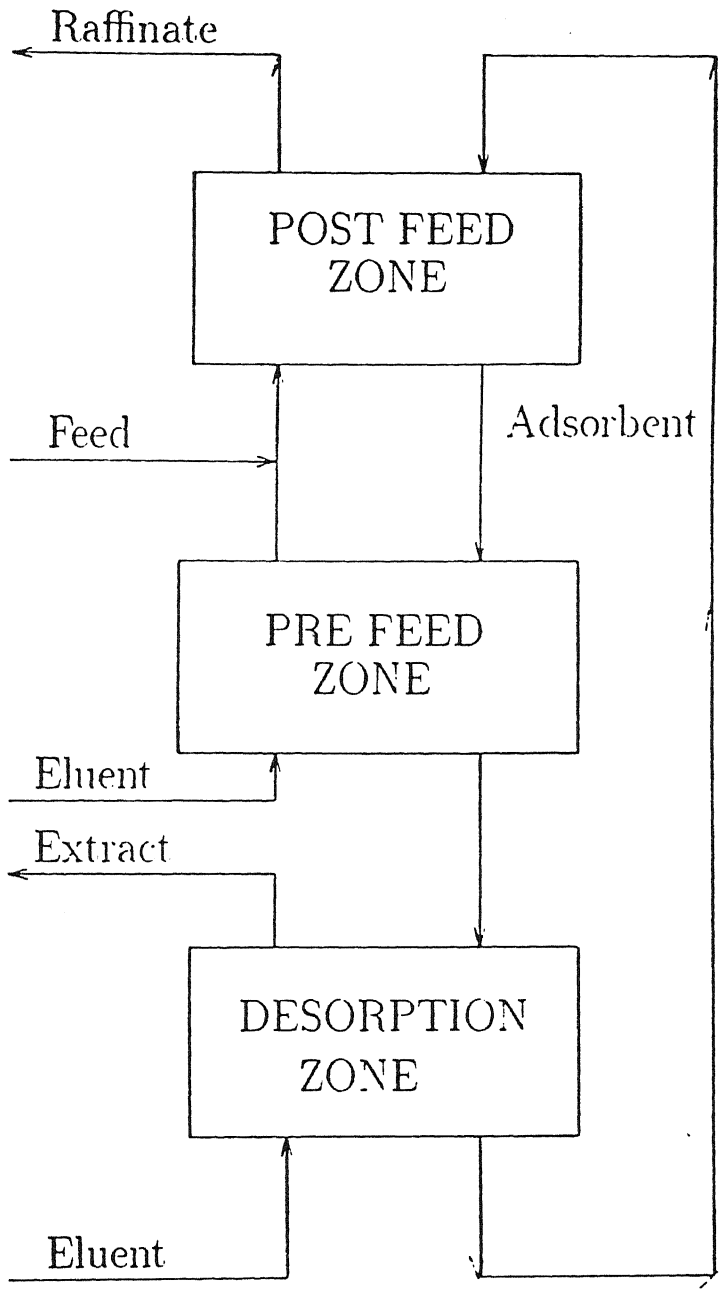


Fig. 2.4 : Principle of operation of SCCR 4

a concentration profile in accordance with the final steady state. In general, it was found that it takes about 10 cycles to reach a quasi-steady state and glucose (less favorably adsorbed component) reaches steady state earlier than fructose. Ching et.al. (37) have extended these transient studies for accounting for axial dispersion and using orthogonal collocation technique.

All the previous studies were carried out under isothermal conditions. The concentration of product streams were considerably lower than the feed concentration for linear systems. Ching and Ruthven (38) explored the feasibility of producing a concentrated extract (fructose) by non-isothermal process. Apart from fructose and glucose separation, the continuous counter-current adsorber experiments were performed with other systems. Ching and Ruthven (39) studied a non-linear system consisting of MEA and water. Hashimoto et. al.(40) used a simulated moving bed with three zones to fractionate L-phenylalanine and NaCl mixture. Fish et. al. (41) have investigated separation of trimethyl-cyclohexane and trymethylbenzene.

Ching et.al. (42) have studied the continuous separation of three carbohydrate mixtures (fructose-dextran), raffinose-dextran and fructose-raffinose using a simulated counter-current process with silica gel as the sorbent and deionized water as the eluent. The behaviour of the simulated counter-current process was simulated theoretically by representing the process in terms of an equivalent true counter-current system. A good fit to the experimental data was obtained when the process was configured in the four section mode. Fish et.al.(41) investigated a steady-state, dispersionless, adsorption equilibrium, plug-flow model of a counter-current moving bed chromatographic moving bed separator. The flux of the constituents of the binary mixture was examined via concentration phase plane plots, which reveal a complex behaviour depending on the parameter 6, the ratio of solid and fluid phase flow of the mobile phase. Numerical simulations with the finite mass transfer model reveal an

optimum operating condition.

Sarmidi et.al.(43) carried out successfully the simultaneous biochemical reaction and separation for the first time in a continuous rotating annular chromatograph (CRAC) by inverting sucrose to glucose and fructose using the enzyme invertase. Numerical simulation for the combined biochemical reaction and separation on a CRAC has also been carried out. the model was solved using a finite difference method and the results indicate a good agreement between the experimental and the predicted elution concentration profile. Niranjan (20) and Prasad (44) provide detailed literature review about high fructose syrup and simulated moving bed operation.

A recent detailed review of the literature on adsorptive separation has been discussed by Ruthven et.al. (45).

Chapter 3

Experimental Study

3.1 Materials used:- Materials used in this study are described below.

3.1.1 Chemicals :- All the chemicals used in this study were reagent grade. D-glucose was obtained from M/s Indian Drugs and pharmaceuticals Ltd. Fructose was supplied by M/s Loba Chemie and calcium chloride (fused) was supplied by M/s Ranbaxy Laboratories. Double distilled water was used throughout the experimental analysis.

3.1.2 Adsorbents :- A variety of cation exchange resins of polystyrene cross linked with divinyl benzene were prepared by M/s Ion Exchange India Ltd. Bombay for the specific needs of this study.These resins were in H^+ form.They were converted to Ca^{+2} form before using them in this studies.

3.2 Method of analysis:- A high performance liquid chromatograph(HPLC) was used to analyze the test samples. A Brief specification of the liquid chromatograph is given in the following.

Specification of the H.P.L.C. system:- The instument manufactured by M/s Shimadzu Corporation , Japan equipped with a carbohydrate column,Refractive index detector,column oven and data module was used in the present studies. The column was kept at 80^0C.Pure water was used as solvent.A constant temperature water bath was used to maintain the solvent temperature at 80^0C. Detailed specifications are given below:-

Detector : Refractive Index (RID-6A)

Column : Shimpak SCR 101(C)

Guard column : SCR(C)

Column Temperature : 80^0C

Operating pressure : 60 kg / cm^2

Solvent flowrate : 1 ml/min.

3.3 Experimental setup for the fixed bed :

The glass columns of various diameters fitted with a control valve at the bottom were used. A piece of glass wool kept at the bottom worked as support to the resins. The assembly was fixed vertically to a steel structure on the work-bench with the help of clamps. The flow of fluid could be regulated with the help of a control valve. A schematic arrangement of the fixed bed column is shown in the fig. 3.1.

Procedure :-

The column was filled with pertinent resins carefully. The resin bed was washed with distilled water several times. The resins were converted to Ca^{+2} form with a use of a dilute solution of calcium chloride till the solution coming out of the column was no longer acidic. After treating with calcium chloride, the bed was again washed with distilled water to remove the residual calcium chloride in the bed. the resins were always kept submerged in water. The water level was kept above resin bed to avoid entry of air bubbles inside the bed.

First the void volume of the bed is determined by passing free water through the bed. Then the glass column was again filled with water and air bubbles are removed completely by shaking the bed. Then the flowrate through the bottom valve is fixed throughout the experiment so that bottom (i.e. the effluent) flowrate remained constant. The water is rejected until it comes to the top level of the bed. At that instant, the solute solution is introduced from an overhead graduated burette at a flowrate equivalent to the outflow of the water from the column. This can be achieved by manipulating the burette valve.

To study the breakthrough curve, after an amount of solution equal to the void volume was drained out of the column, samples of the eluent stream were collected from the column at intervals of 2-4 minutes. They were analyzed using HPLC. The ratio of solute concentration(C_t) from the column outlet at any time "t" to its initial concentration "C_i " is a measure of the adsorption potential of the adsorbent.

For the glucose-fructose separation, the solution is passed through the bed and the filled the whole column length upto top level of the bed. At that instant eluent (i.e. water) is passed through the bed and the effluents were collected at the intervals of 2-4 minutes. The effluent is analyzed using HPLC for the glucose and fructose content.

3.4 Design of the simulated moving bed apparatus:

The experimental apparatus is as shown in the fig 2.3 . The plexi glass column of 45 mm. diameter and 360 cm. height was used for this purpose.The column was divided into 12 equal parts axially and four nozzles were grooved for tube connections to a multi-port rotary valve. The rotary valve is the most important equipment in the whole setup. The feed, desorbent, extract and raffinate points in the column are fixed and defined by the material balance and the experiments carried out in fixed bed operation. The operational methodology involves the switching of rotary valve by 30^0(360/12), after certain fixed time called switch time. This enables the switching of feed, desorbent, extract and raffinate points by about 300 mm. each in the direction of fluid flow. the whole cycle is completed after 12 switchings. The feed and desorbent are passed to the column through the rotary valve. the extract and raffinate are received through the rotary valve simultaneously. Rotary valve takes care that all the four streams should not intermix with each other inside the valve.

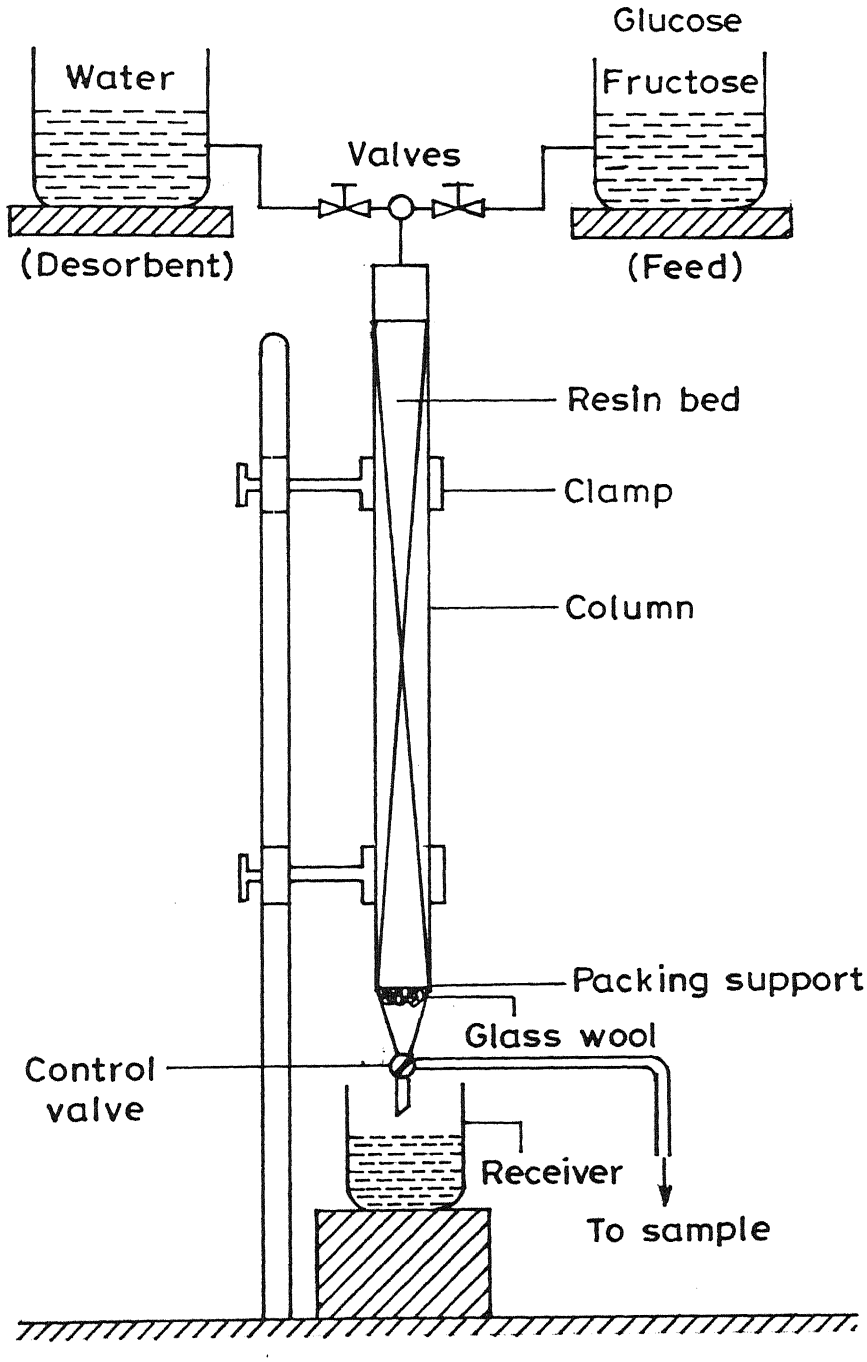


Fig. 3.1 : The experimental setup for fixed bed operation

Chapter 4

Modeling

There are many stages between a concept and its practical implementation. Simulation and modeling provide cheaper alternatives to test a viability of a concept. With the advent of the high speed computers, simulating the behavior of the actual process on the computer, either numerically or graphically is much faster and efficient. Hence, computer simulation was undertaken for modeling the simulated moving bed.

4.1 Basic principles underlying the modeling of simulated moving bed adsorber:

Although the simulated moving bed adsorber does not include the real movement of the adsorbent particles, the operation is more clearly understood in terms of a hypothetical moving bed adsorber (refer fig. 4.1). The actual movement of the adsorbent may cause the abrasion of the adsorbent and the channelling of the liquid flow. So without any actual movement of the adsorbent, the counter-current movement of the liquid and adsorbent can be simulated in the simulated moving bed(SMB) operation. To design simulated moving bed adsorber however, we have to study the corresponding fixed bed operation and use the parameters calculated to design the SMB operation. The more popular approach is that the modeling of the fixed bed adsorber is done first, then the boundary conditions are added for the simulated moving bed operation, because in SMB the whole unit works as if the fixed beds are arranged in series except during switching operation. This model mostly works in the transient mode. It expresses the actual mode of operation and is useful in the calculation of transient change in the concentration profiles in the adsorber. But here

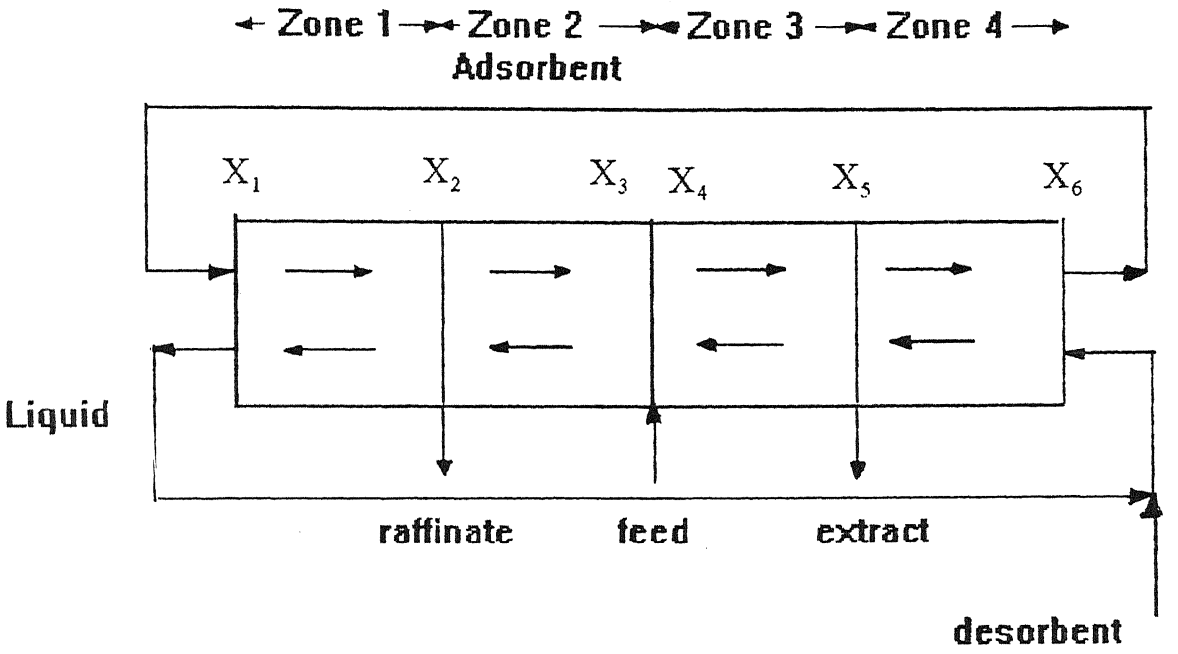


Fig. 4.1 : Schematic representation of a hypothetical moving bed adsrber

we will discuss a continuous or hypothetical moving bed model which is based on the hypothetical movement of adsorbent. That is nearly an equivalent operation of the SMB adsorber is assumed in that the counter-current motion of adsorbent and the fluid takes place. Niranjan (20) attempted the modeling of SMB using hypothetical moving bed, but he also included the dispersion effects in his model. Prasad (44) attempted the modeling and simulation of S.M.B. using transient or intermittent moving bed model. Hashimoto et.al.(35) developed two models one based on the hypothetical moving bed and another actual mode of operation of the unit.

4.2 Modeling of the Simulated moving bed : (20,35,44)

The following assumptions were made for modeling of the SMB.

1) The adsorption isotherms of glucose and fructose are both linear and independent of each other.
2) The axial dispersion can be ignored.
3) The overall mass transfer coefficients of glucose and fructose are same and do not depend on the rate of liquid flow.
4) The adsorption is carried out isothermally.
5) The rate of adsorption is controlled by external mass transfer.

In the hypothetical moving bed, the mass balance is done in any zone n as shown in fig. 4.2.

The terms used are :

u_s = hypothetical velocity of adsorbent= L_A / T

where L_A=length of each column

T=switch time

u_n =superficial velocity of the liquid flow

K→ component

n→ zone

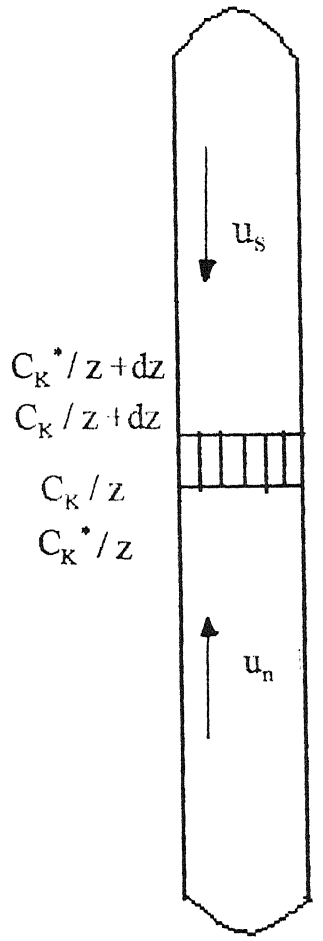


Fig. 4.2 : Mass balance at any zone n in hypothetical moving bed

C_K =concentration of component in the mobile phase i.e. fluid phase

C_K^* =concentration of component in the stationery phase i.e. solid phase

$z \rightarrow$ axial distance

$A \rightarrow$ cross-sectional area of the bed

ϵ = bed voidage

m_K = distribution coefficient---

K_f = overall mass transfer coefficient (m/s)

a_V = specific surface area (m^2/m^3 of the bed)

In the control volume $A\Delta z$,we have

Rate of Input - Rate of output = Rate of accumulation

$$(u_n A C_K / {}_z + u_s m_K A(1-\epsilon) C_K^* / {}_{z+dz}) - (u_n A C_K / {}_{z+dz} + u_s m_K A(1-\epsilon) C_K^* / {}_z) = A\Delta z\, \epsilon\, \delta C_K / \delta t + A\Delta z (1-\epsilon)\, \delta C_K^* / \delta t \text{ ----------(1)}$$

Dividing by $A\Delta z$ and applying $\Delta z \rightarrow 0$,we have

$$u_n\, dC_K / dz - u_s m_K (1-\epsilon)\, dC_K^* / dt = \epsilon\, \delta C / \delta t + (1-\epsilon)\, \delta C_K^* / \delta t \text{ --------(2)}$$

Note that the dispersion coefficient is absent from the above equations as axial dispersion is ignored.The hypothetical velocity of the adsorbent(u_s) was simply defined as L_A / T i.e. the length of the column divided by the switch time.The superficial velocity in the hypothetical moving bed (u_n) can be defined as

$$u_n = v_n - \epsilon u_s \text{ ----------(3)}$$

.where v_n = superficial velocity in the fixed bed.

This expression comes due to the fact that, in fixed bed operation, the velocity of the adsorbent is zero.But in hypothetical moving bed, the adsorbent is hypothesized to be moving in the velocity u_s which has to be compensated by the superficial velocity of the liquid. Also u_s is multiplied by the bed voidage (ϵ) as the superficial velocity is related only to liquid flow.Hence the superficial velocity in hypothetical bed is always less than that in the fixed bed.

At steady state, $\delta C_K/\delta t = 0$, $\delta C_K^*/\delta t = 0$

$\therefore u_n dC_K / dz - u_S m_K(1-\epsilon) dC_K^*/dz = 0$ ----------(4)

If the adsorption rate is controlled by the external mass transfer, it can be written as

$u_n(dC_K/dz) = K_f a_V (C_K - C_K^*)$ ----------(5)

From (4) and (5),

$u_S m_K(1-\epsilon) dC_K^*/dz = K_f a_V (C_K - C_K^*)$ ----------(6)

These equations are solved using the boundary conditions to get the concentration profiles.

4.3 Solution of the problem:

Consider the zone n again as shown in the fig. 4.3.

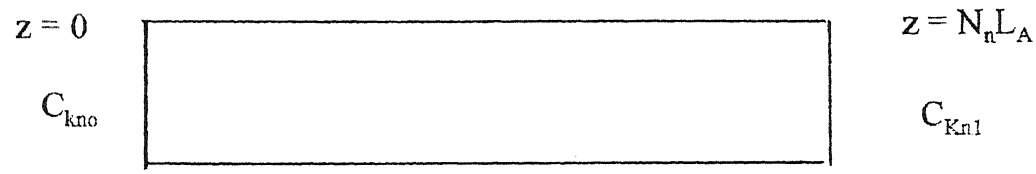


Fig. 4.3 : Boundary conditions at any zone n in hypothetical moving bed

As shown in the figure above we can find the outlet concentration explicitly using inl concentrations which are known.

At $z = 0$, $C_K = C_{Kn0}$

$z = N_n L_A$, $C_K = C_{Kn1}$

where N_n = number of columns in the zone n

where 0→ entrance and 1→ exit.

Dividing equation(5) by equation (6),

$(u_n/(1-\epsilon)m_K u_S) dC_K = dC_K^*$

Integrating ,

$$\{ u_n /(1- \epsilon)m_K u_S \} \int_{C_{Kn0}}^{C_{Kn1}} dC_K = \int_{C_{Kn0}}^{C_{Kn1}} dC_K^*$$

Let $\beta_{nK} = u_n / (1- \epsilon)m_K u_S$

$\therefore \beta_{nK} (C_{Kn1} - C_{Kn0}) = C^*_{Kn1} - C^*_{Kn0}$

$\therefore C^*_{Kn1} = C^*_{Kn0} + \beta_{nK} (C_{Kn1} - C_{Kn0})$

$\therefore C^*_{Kn1} = (C^*_{Kn0} - \beta_{nK} C_{Kn0}) + \beta_{nK} C_{Kn1}$

Let $\lambda = C^*_{Kn0} - \beta_{nK} C_{Kn0}$

$\therefore C^*_{Kn1} = \lambda + \beta_{nK} C_{Kn1}$ ----------(7)

From equation (5),

$dC_K / (C_K - C_K^*) = (K_f a_V / u_n) dz$

Putting (7) in above equation and integrating,

$$\int_{C_{Kn0}}^{C_{Kn1}} dC_K / (C_{Kn1} - \lambda - \beta_{nK} C_{Kn1}) = (K_f a_V / u_n) \int_0^{N_n L_A} dz = (K_f a_V / u_n) N_n L_A$$

where $N_n L_A$ = length of zone n

Let $\alpha_n = K_f a_V L_A / u_n$

$$\therefore \int_{C_{Kn0}}^{C_{Kn1}} dC_K / \{(1- \beta_{nK})C_{Kn1} - \lambda\} = \alpha_n N_n$$

$$\therefore \left[\ln\{(1- \beta_{nK}) - \lambda\}/ (1- \beta_{nK})\} \right]_{C_{Kn0}}^{C_{Kn1}} = \alpha_n N_n$$

$$\therefore \quad 1/(1-\beta_{nK})\,[\ln\{(1-\beta_{nK})C_{Kn1}-\lambda\}-\ln\{(1-\beta_{nK})C_{Kn0}-\lambda\}]=\alpha_n N_n$$

$$\therefore \quad \ln\frac{\{(1-\beta_{nK})C_{Kn1}-\lambda\}}{\{(1-\beta_{nK})C_{Kn0}-\lambda\}} = N_n\alpha_n(1-\beta_{nK})$$

$$\therefore \quad \frac{\{(1-\beta_{nK})C_{Kn1}-\lambda\}}{\{(1-\beta_{nK})C_{Kn0}-\lambda\}} = \exp\{N_n\alpha_n(1-\beta_{nK})\}$$

Putting the value of λ and proper arrangements, we have

$$C_{Kn1}\quad\frac{\exp\{\alpha_n(1-\beta_{nK})N_n\}-\beta_{nK}}{1-\beta_{nK}}C_{Kn0}+\frac{1-\exp\{\alpha_n(1-\beta_{nK})N_n\}}{1-\beta_{nK}}C^*_{Kn0}\text{---(8)}$$

Similarly,

$$C^*_{Kn1}=\frac{\beta_{nK}[\exp\{\alpha_n(1-\beta_{nK})N_n\}-1]}{1-\beta_{nK}}C_{Kn0}+\frac{1-\beta_{nK}\exp\{\alpha_n(1-\beta_{nK})N_n\}}{1-\beta_{nK}}C^*_{Kn0}\text{-(9)}$$

Also at zone boundaries, we have

$C_{K21}=C_{K10}$----------(10)

In the above equation, the first digit denotes the zone number and the second digit denotes entry or exit point.

$V_fC_{Kf}+V_3C_{K31}=V_2C_{K20}$----------(11)

$C_{K41}=C_{K30}$ ----------(12)

$V_1C_{K11}=V_4C_{K40}$----------(13)

We also define a new variable $C_{K*}=C_K-C^*_K$

The equations were put in matrix form.

$$\begin{bmatrix} -E & 0 & 0 & 0 & 0 & D \\ A_1 & -E & 0 & 0 & 0 & 0 \\ 0 & A_2 & -E & 0 & 0 & 0 \\ 0 & 0 & F & -E & 0 & 0 \\ 0 & 0 & 0 & A_3 & -E & 0 \\ 0 & 0 & 0 & 0 & A_4 & -E \end{bmatrix} [\, X_1\ X_2\ X_3\ X_4\ X_5\ X_6 \,]^T$$

$$= [\, 0\ 0\ 0\ f\ 0\ 0 \,]^T$$

where $X_i = [\, C_{Ki}\ C^*_{K^*i} \,]^T$

$$A_n = \begin{bmatrix} 1 & \dfrac{1 - \exp\{\alpha_n(1-\beta_{nK})N_n\}}{1-\beta_{nK}} \\ 0 & \exp\{\alpha_n(1-\beta_{nK})N_n\} \end{bmatrix}$$

$$D = \begin{bmatrix} u_4/u_1 & 0 \\ 1 - u_4/u_1 & 1 \end{bmatrix}$$

$$F = \begin{bmatrix} u_2/u_3 & 0 \\ 1 - u_2/u_3 & 1 \end{bmatrix}$$

$$f = [\, C_{Kf}\, u_f / u_3 \qquad -Ckfuf/u3 \,]^T$$

$$E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

These equations are solved using Gauss-Jordan technique to obtain the steady state concentration profiles in the adsorber.

Chapter 5

Results And Discussions

5.1 Separation of glucose and fructose in a fixed bed apparatus :

Preliminary studies conducted by Niranjan(20) indicated resins RDL-90-7 and RDL-90-8 to be good adsorbents for separation of glucose and fructose. A feed composition of 50:50 glucose and fructose was used.The effects of flowrate, bed height and feed concentration were studied.

Definitions of the terms used in the analysis of the performance of fixed bed apparatus are discussed in the following.

1) Actual separation time: It is the time taken for fructose and glucose to separate after the void volume has been displaced by the feed and elution is started.

2) Total separation time : It is the total time taken for the separation process to complete starting from the feed input to the last drop of the fructose eluted from the column. It signifies the cost effectiveness of the process, more explicitly. It also enable to calculate the amount of H.F.S. obtained in one run. Total separation time is always greater than actual separation time.

3) Resolution(separation factor) : It is the ratio of distance of the fructose peak from the starting (zero) time of the actual separation time to the corresponding time for glucose.

4) Fructose rich fraction(extract-H.F.S.) : It is the fructose rich fraction which is the product of our concern. Hereafter, the words extract and H.F.S. are used interchangeably.

5) H.F.S. purity : It is the fraction of fructose content in the extract. Generally, H.F.S. purity is specified and system is designed to obtain the desired purity level.

6) Fructose recovery in H.F.S. w.r.t. feed : It is the ratio of the fructose content in the extract to that in the feed.

7) H.F.S. molar rate (mol/min) : It is the total number of moles of H.F.S. processed in the total separation time.

8) Desorbent requirement : It is the desorbent required for the separation process to complete. It is found by multiplying actual separation time and the flowrate.

5.1.1 The effect of flowrate :

Evidently, flowrate is an important parameter in fixed bed operations. Other parameters being constant, with an increase in flowrate the separation time decreases. As noted from the results given in table 5.2, for the same level of H.F.S. purity, H.F.S. fraction remains constant. That is the flowrate does not have influence on the H.F.S. fraction of the effluent. Howeover, the effect of flowrate on fructose recovery in H.F.S. with respect to feed is noted to be substantial. The fructose recovery is drastically low in run 3. This is because of the fact that the resolution is highest in run 1 and decreases progressively with flowrate. Further, as shown in fig. 5.1, at low flowrate(run no. 1), the glucose and fructose start lately and are more concentrated in the extract zone. The H.F.S. molar rate is found to be higher in run 3 than run 2 which is more than run than run 1, because of the shorter separation time. At higher flowrates, the desorbent(water in this case) requirement increases. For commercial operations this may prove to be crucial if desorbent is expensive.

Thus, the flowrate may be chosen according to the requirements. The results of run 2 are reasonably good as compared to other runs.

5.1.2 The effect of concentration :

The effect of variations in the concentration of the feed on the performance of

Table 5.1 : Important parameters for the effect of flowrate

Parameter	run 1	run 2	run 3
Resin	RDL-90-7	RDL-90-7	RDL-90-7
Feed mixture conc.(mol/lit.)	0.05	0.05	0.05
Flowrate(ml/min.)	4.7	10	22
void volume(ml)	175	175	175
Bed height(cm)	28	28	28
Bed diameter(cm)	5	5	5
Temperature(^{0}C)	20	20	20

Table 5.2 : The effect of flowrate on fixed operation

Parameter	run 1	run 2	run 3
Flowrate (ml/min)	4.7	10	22
Actual separation time (min)	192	100	50
Total separation time (min)	237	117.5	57
H.F.S. fraction (%)	68	68	68
H.F.S. purity (%)	61.1	61.24	61.05
Fructose recovery in extract(H.F.S.) w.r.t. feed (%)	88.25	70.03	57.56
H.F.S. molar rate (gmole/min.)	2.66×10^{-5}	4.26×10^{-5}	7.24×10^{-5}
resolution	1.434	1.38	1.229
Desorbent requirement(in ml.)	902.4	1000	1100

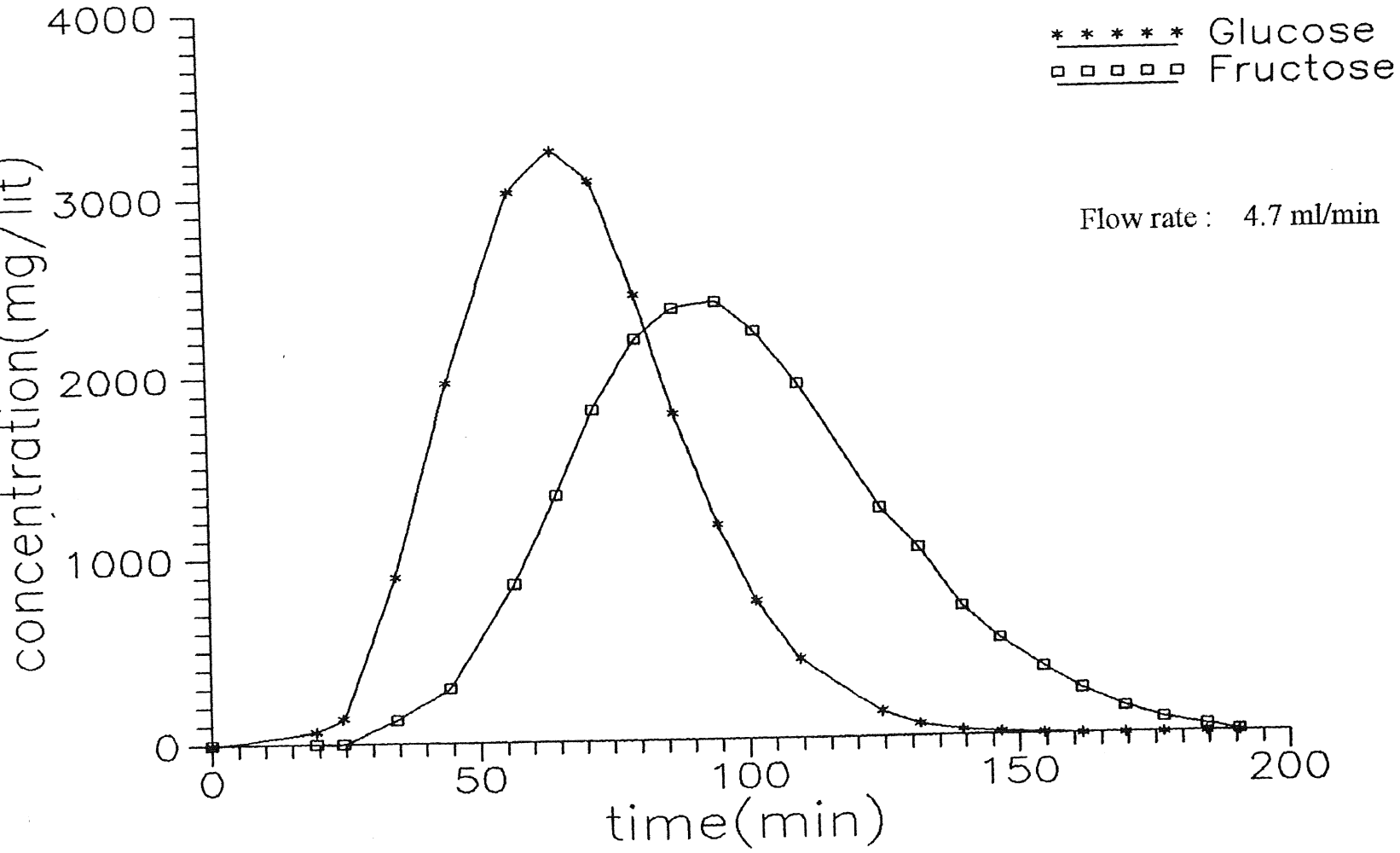


Fig. 5.1 : Effect of flowrate on fixed bed operation (run 1)

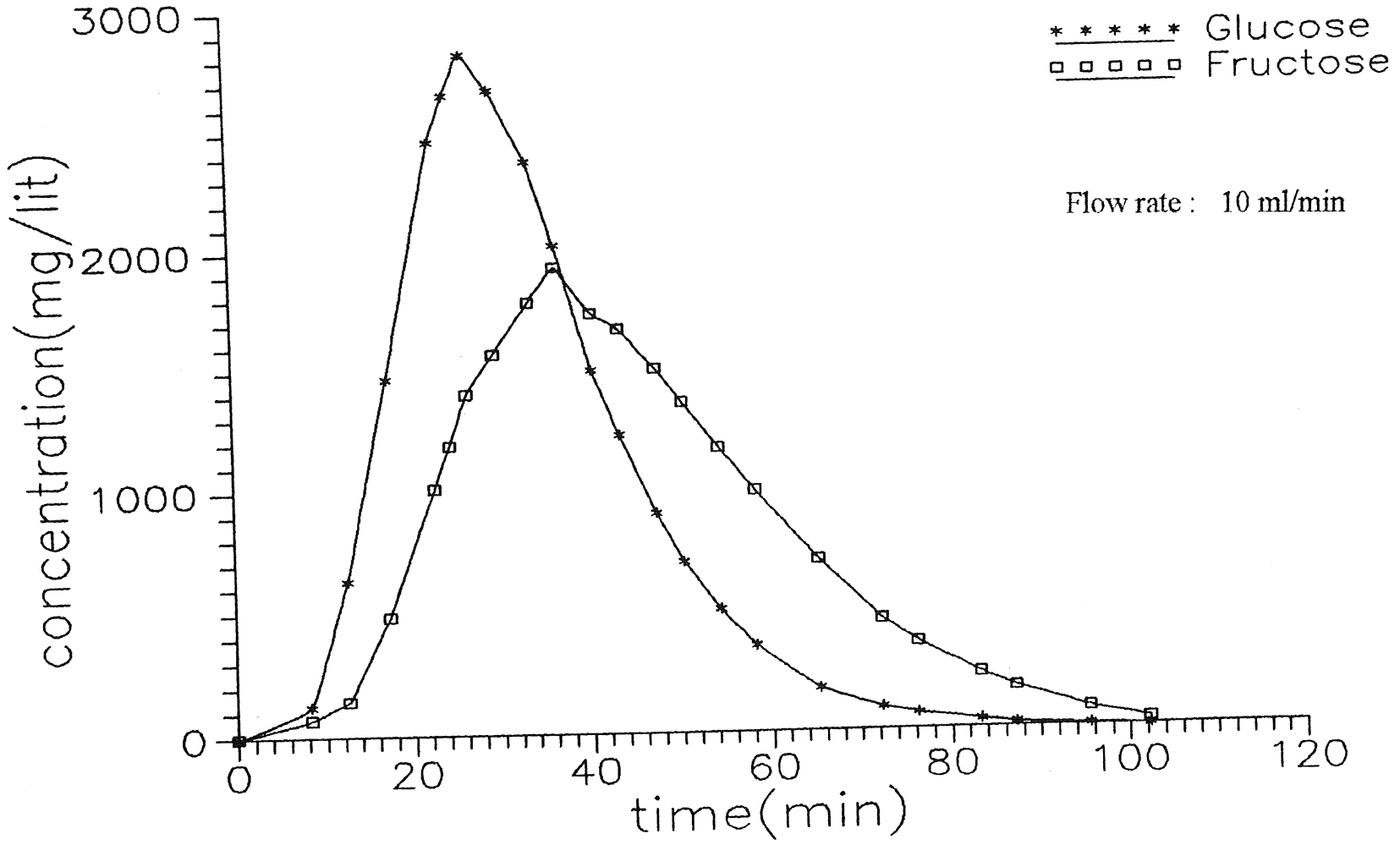


Fig. 5.2 : Effect of flowrate on fixed bed operation (run 2)

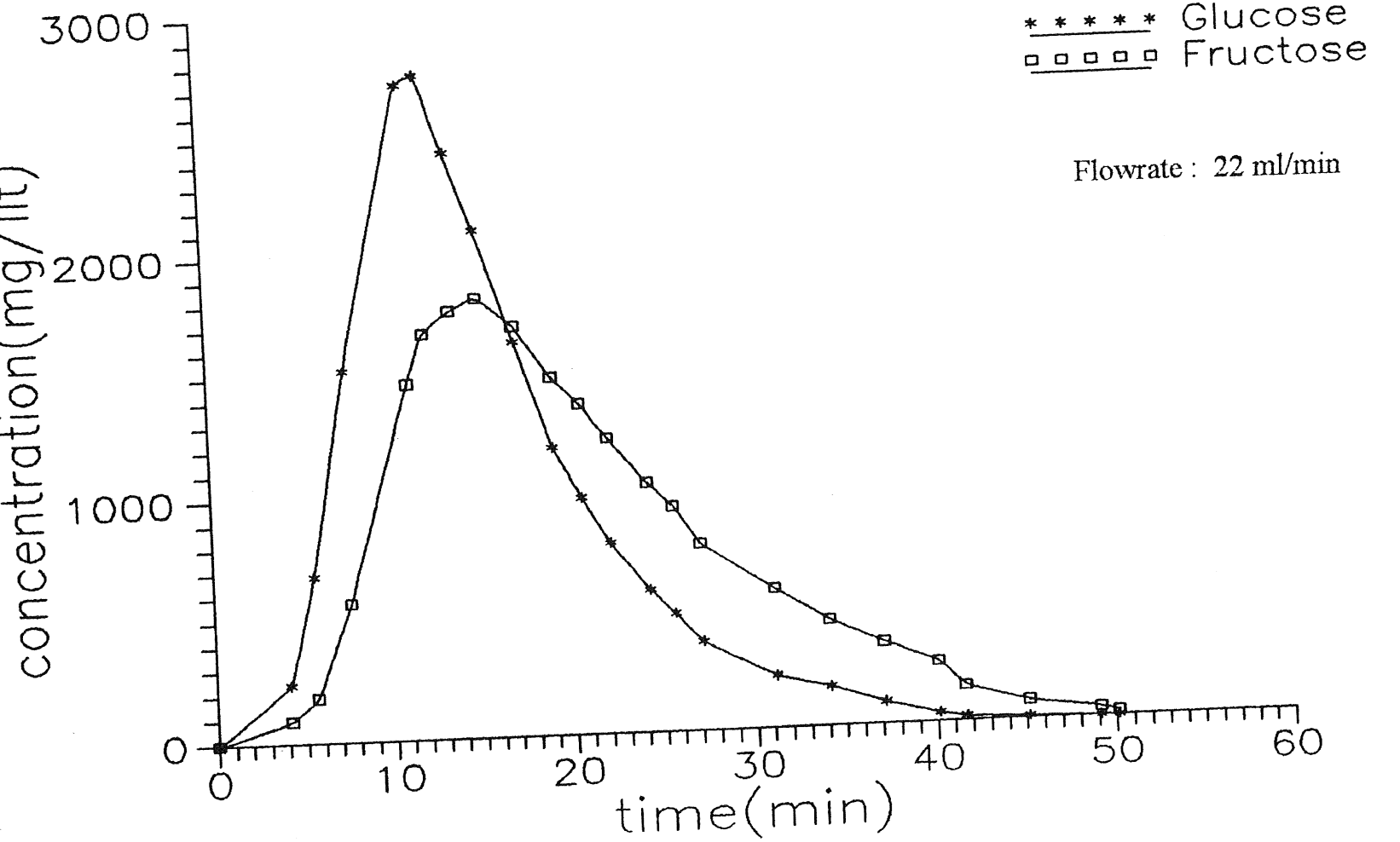


Fig. 5.3 : Effect of flowrate on fixed bed operation (run 3)

Table 5.3 : Important parameters for the effect of concentration

Parameter	run 4	run 5	run 6
Resin	RDL-90-7	RDL-90-7	RDL-90-7
Feed mixture conc.(mol/lit)	0.1	0.2	0.4
Flowrate (ml/min)	4.1	4.1	4.1
Void volume (ml)	25	25	25
Bed height (cm)	40	40	40
Bed diameter (cm)	1.5	1.5	1.5
Temperature (^{0}C)	20	20	20

Table 5.4 : The effect of concentration on fixed bed operation

Parameter	run 4	run 5	run 6
Feed mixture conc. (mol/lit)	0.1	0.2	0.5
Actual separation time (min)	34.5	34	34
Total separation time (min)	40.6	40	40
resolution	1.225	1.272	1.27
H.F.S.fraction (%)	60.87	62.5	61.76
H.F.S. purity (%)	62.46	62.11	62.32
Fructose recovery in extract(H.F.S.) w.r.t. feed (%)	61.49	64.02	60.403
H.F.S. molar rate (gmol/min)	3.03×10^{-5}	6.44×10^{-5}	1.21×10^{-5}
Desorbent requirement (ml)	141.45	139.4	139.4

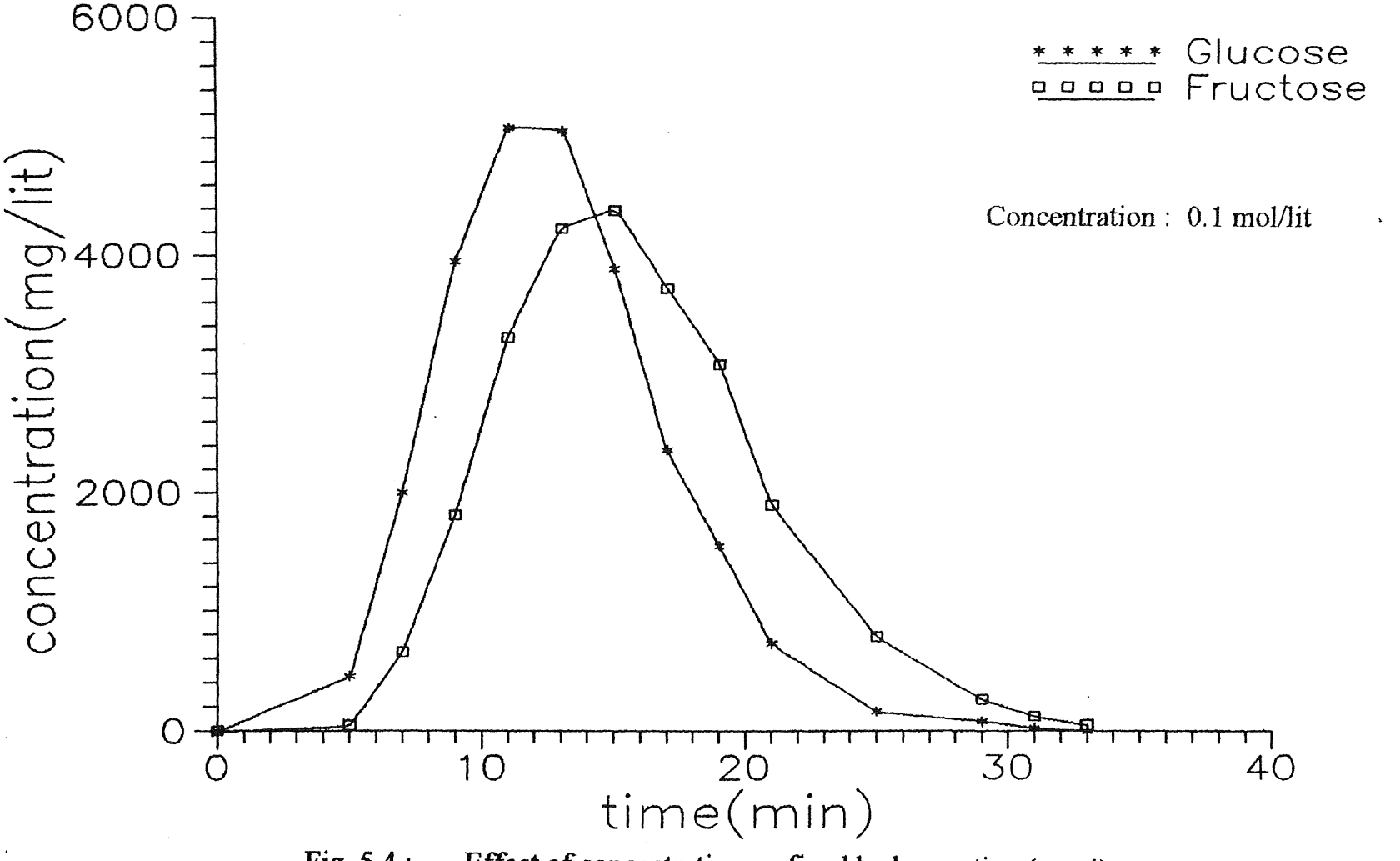


Fig. 5.4 : Effect of concentration on fixed bed operation (run 4)

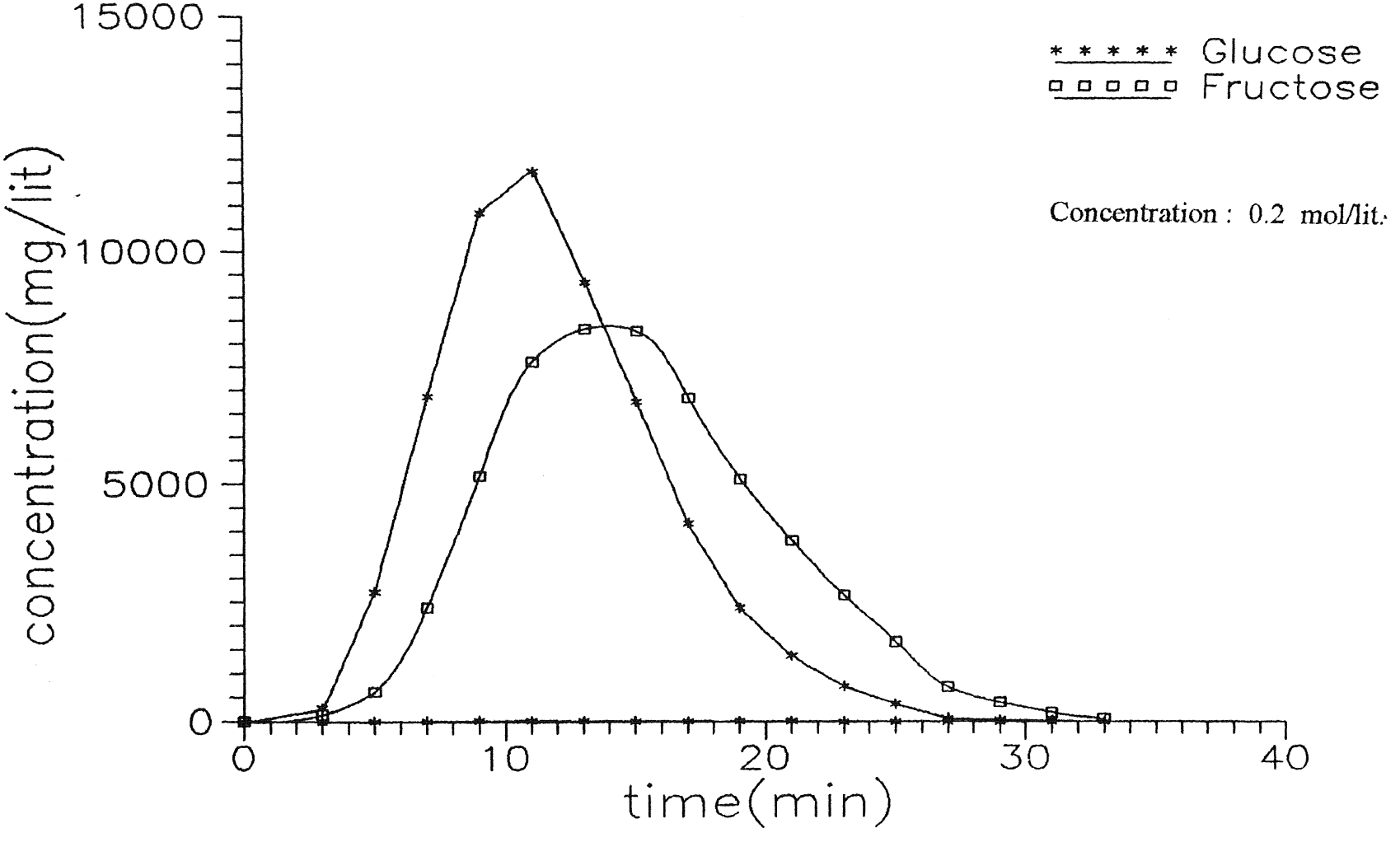


Fig. 5.5 : Effect of concentration on fixed bed operation (run 5)

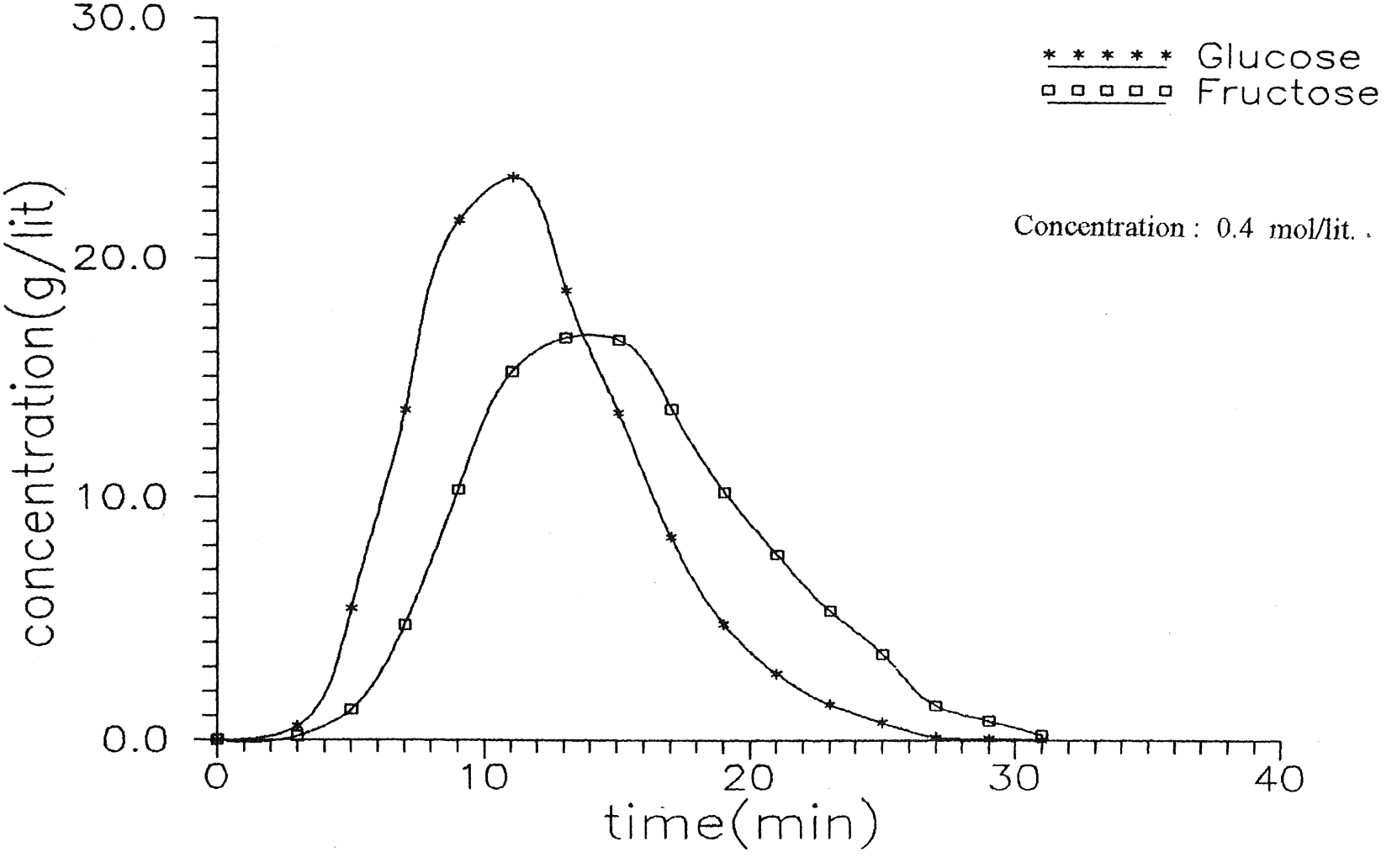


Fig. 5.6 : Effect of concentration on fixed bed operation (run 6)

the fixed was observed for the parameters given in the table 5.3. The concentration of the feed was varied from 0.1 to 0.4 gmol/litre.

As seen from the results given in table no. 5.4, the effect of the change in concentration does not have effect on the separation time, resolution, H.F.S. fraction with respect to H.F.S. purity as well as the fructose recovery with respect to the feed. Howeover the product output increases proportionately with an increase in the feed concentration. Howeover, drastic increase in the concentration will affect the adsorptive capacity of the bed and the separation will not occur after the bed gets saturated. It may be pointed out that the isotherm of glucose and fructose is linear within the saturation limit.

5.1.3 The effect of bed-height :

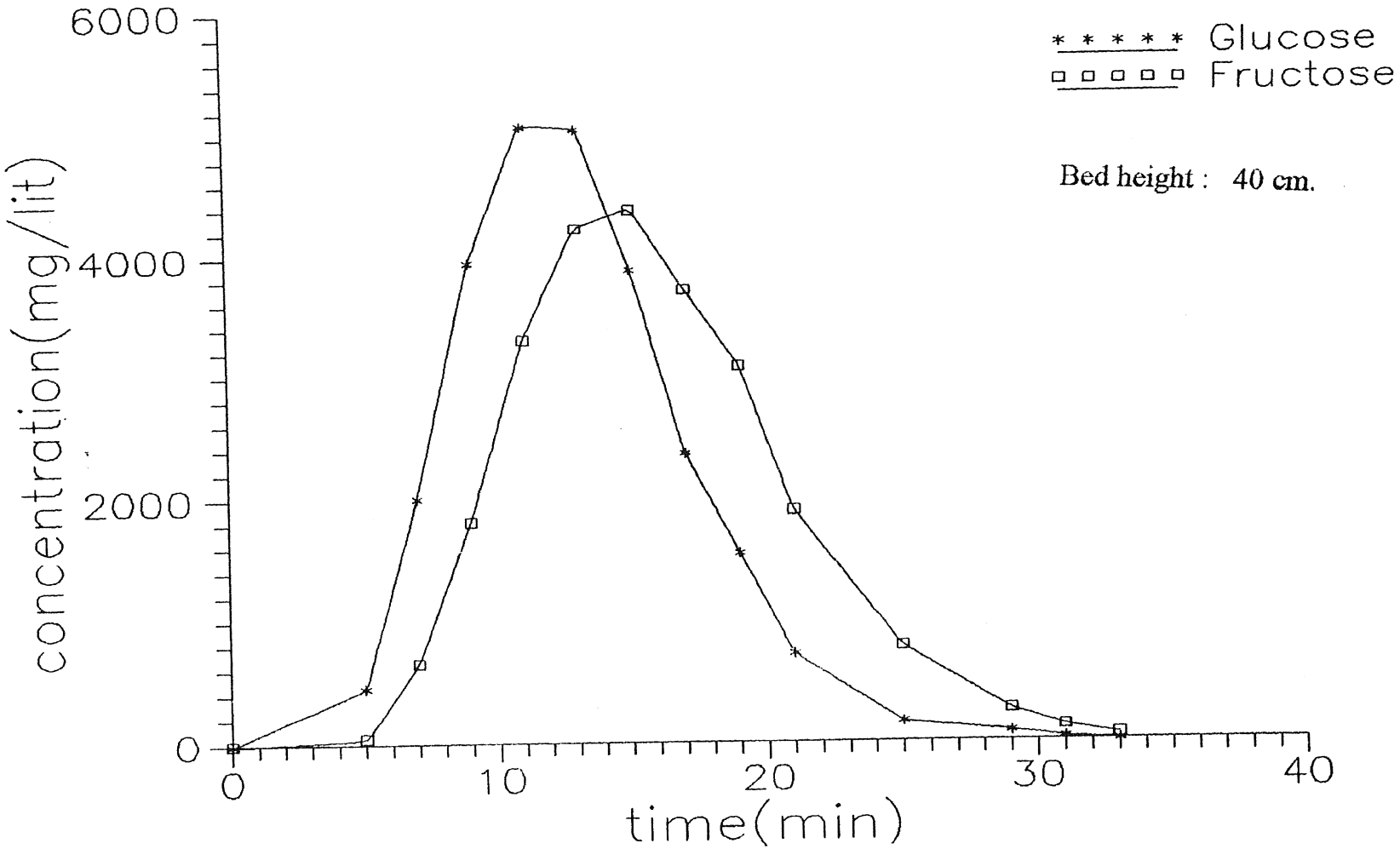
The major parameters studied for observing the effect of bed-height on the column performance are given in table 5.5, The bed-height was varied from 40 to 70 cm. The results are given in table 5.6.As noted from the results, keeping all the parameters constant, there is no appreciable difference in H.F.S. fraction with respect to H.F.S. purity. Also the relative resolution remains constant. But the separation increases with the bed height(see run 7). This is because of the fact that with higher bed heights, the amount of feed to be processed is larger because of greater void-volume.The fructose recovery which is an important parameter, is noted to increase substantially with bed height. Evidently, this is due to the fact that glucose and fructose are more concentrated in the extract zone (in run 7) though both runs have same resolution.The molar rate of H.F.S. is found to increase with bed-height. Howeover the desorbent requirement is higher in run 7 .

Table 5.5 : Important parameters for the effect of bed height

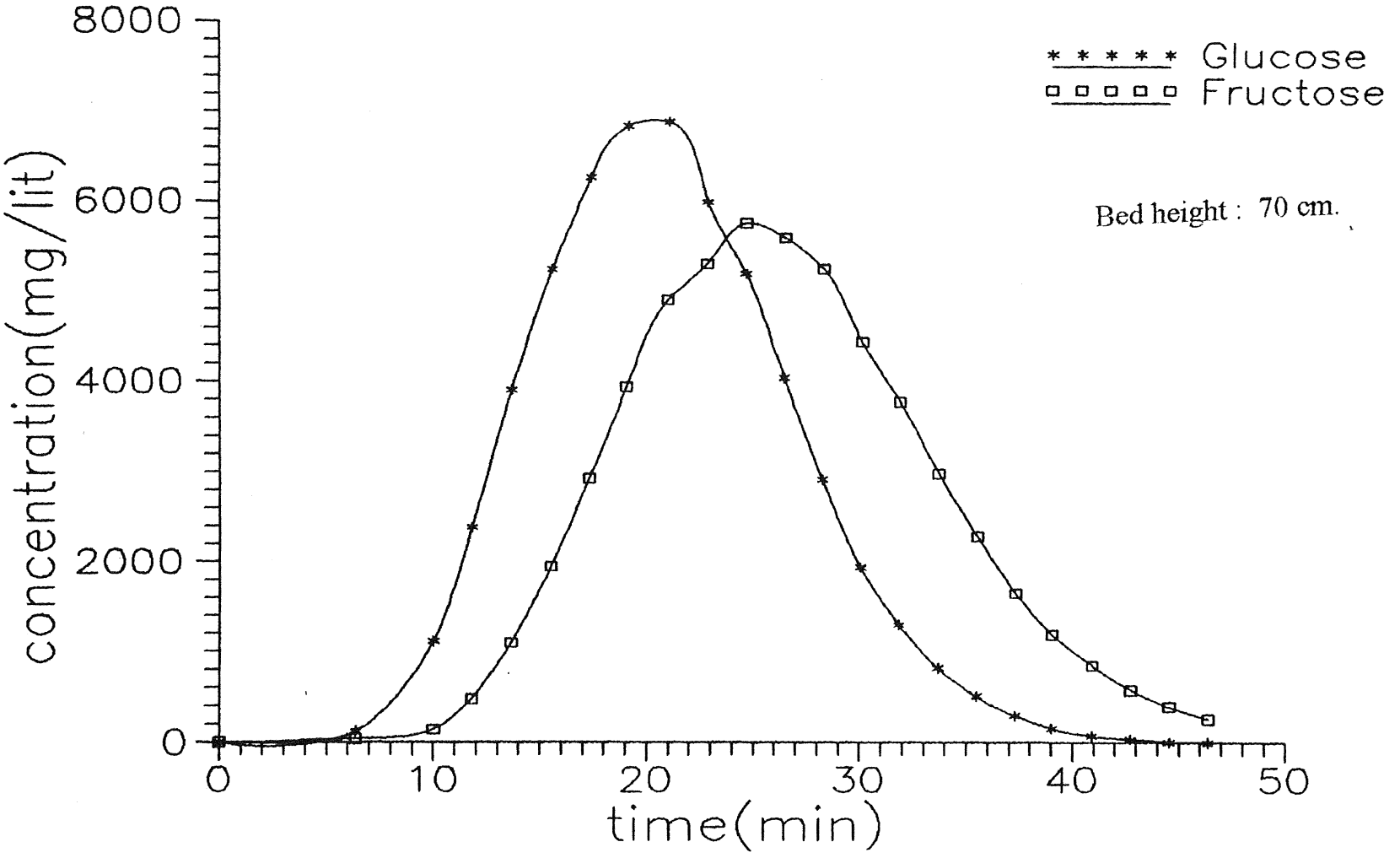
Parameter	run 4	run 7
Resin	RDL-90-7	RDL-90-7
Bed height (cm)	40	70
Feed concentration (mol/lit.)	0.1	0.1
flowrate (ml/min)	4.1	4.1
Void volume (ml)	25	25
Bed diameter (cm)	1.5	1.5
Temperature (^{0}C)	20	20

Table 5.6 : Effect of bed height on fixed bed operation

Parameter	run 4	run 7
Bed height (cm)	40	70
Actual separation time (min)	34.5	52
Total separation time (min)	40.6	63
resolution	1.225	1.235
H.F.S. fraction (%)	60.87	59.61
H.F.S. purity (%)	62.46	62.2
Fructose recovery in H.F.S. w.r.t. feed (%)	61.49	80.52
H.F.S. molar rate (mol/min)	3.03×10^{-5}	4.5×10^{-5}
Desorbent requirement (ml)	141.45	213.2



] 5.7 : Effect of bed height on fixed bed operation (run 4)



5.8 : Effect of bed height on fixed bed operation (run 7)

5.2 Breakthrough curves for glucose and fructose system :

For these studies, adsorption of glucose and fructose on the resin RDL-90-8 was studied. The effect of parameters like temperature and concentration was studied. The breakthrough curves were obtained and they were used to calculate saturation time and equilibrium constant.Using this, we can design a simulated moving bed adsorber.

5.2.1 The effect of temperature :

The effect of temperature on the single component adsorption of glucose and fructose on RDL-90-8 was considered. As shown in fig. 5.9 and fig. 5.10, increase in the temperature decreases the saturation time of the curve. This is because at higher temperatures the adsorptive capacity of the resin decreases. Hence the amount adsorbed was less at higher temperatures. It can also be noted from fig 5.9 and fig. 5.10 that the saturation time in case of fructose is more than that of glucose at any particular temperature. This is due to the preferential adsorption of fructose on the bed as compared to glucose.

5.2.2 The effect of concentration :

The effect of concentration on the single component adsorption of glucose and fructose on RDL-90-8 was studied. The other parameters were kept constant. As shown in the fig. 5.11 and fig. 5.12, an increase in the concentration of the feed shifts the breakthrough curve towards the ordinate. Hence the saturation time decreases with increase in the concentration. this is because an increase in concentration of the feed enhances the rate of adsorption of the solute on the bed. Hence the bed gets saturated faster. Consequently, the eluent concentration approached the feed concentration rapidly. It can also be observed from fig. 11 and fig. 12 that the saturation time in case of fructose is more than that of glucose at any particular concentration. This is due to the preferential adsorption of fructose as compared to glucose.

Table 5.7 : Important parameters for the effect of temperature on adsorption of glucose and fructose

Parameter	run 8,11	run 9,12	run 10,13
Resin	RDL-90-8	RDL-90-8	RDL-90-8
Feed concentration(mol/lit.)	0.05	0.05	0.05
Temperature(^{0}C)	20	30	30
Feed flowrate(ml/min.)	1.2	1.2	1.2
Bed diameter(cm)	1.5	1.5	1.5
Volume of the bed(cm^3)	94.2	94.2	94.2
Bed voidage(ϵ)	0.31	0.31	0.31

Table 5.8 : Results for the effect of temperature on adsorption of glucose and fructose

Parameter	Glucose			Fructose		
	run 8	run 9	run 10	run 11	run 12	run 13
Breakthrough time (min)	26	22	16	34	30	26
Saturation time (min)	54	54	44	58	62	47

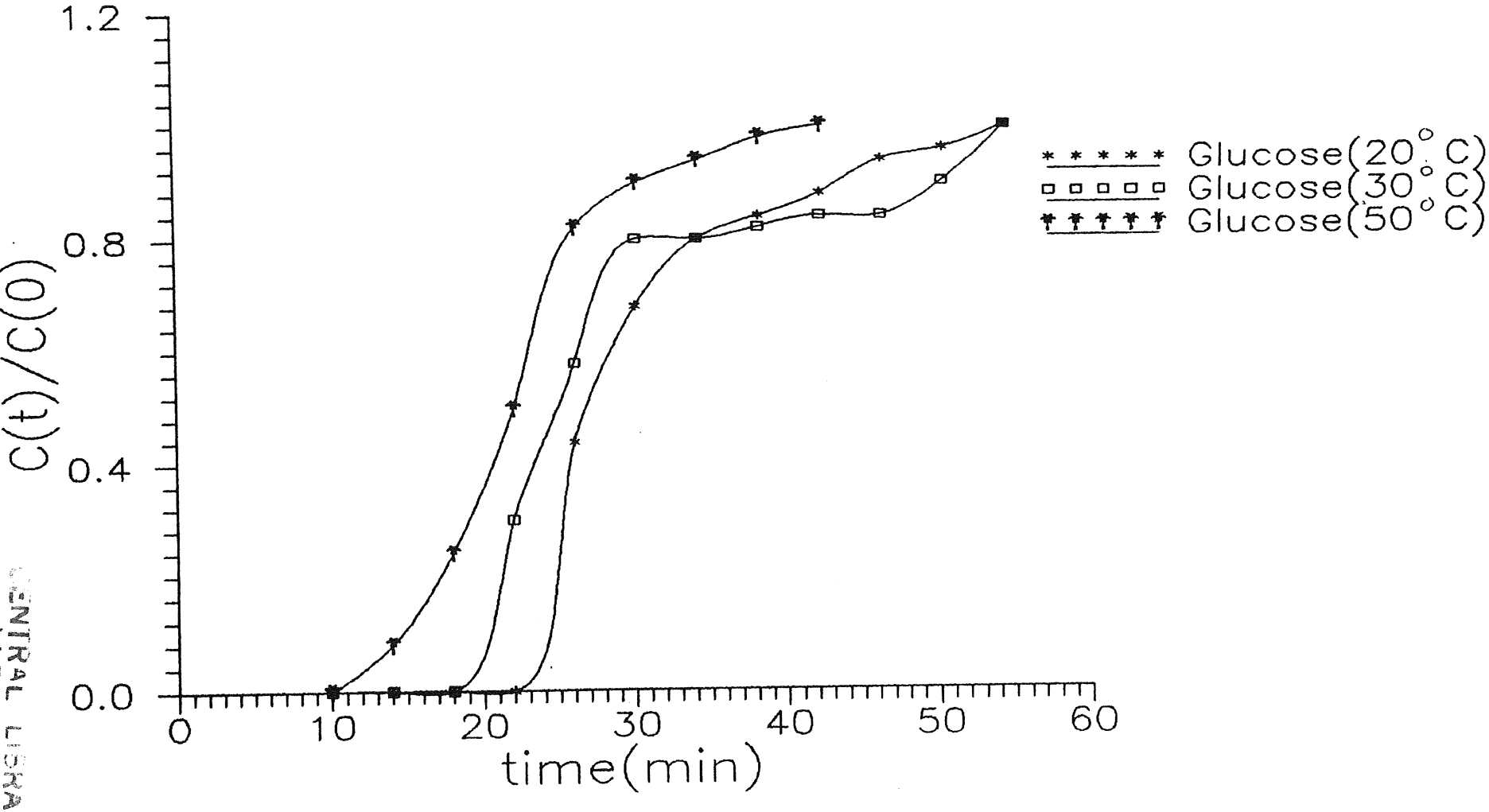


Fig. 5.9 : Effect of temperature on adsorption of glucose (run 8, 9, 10)

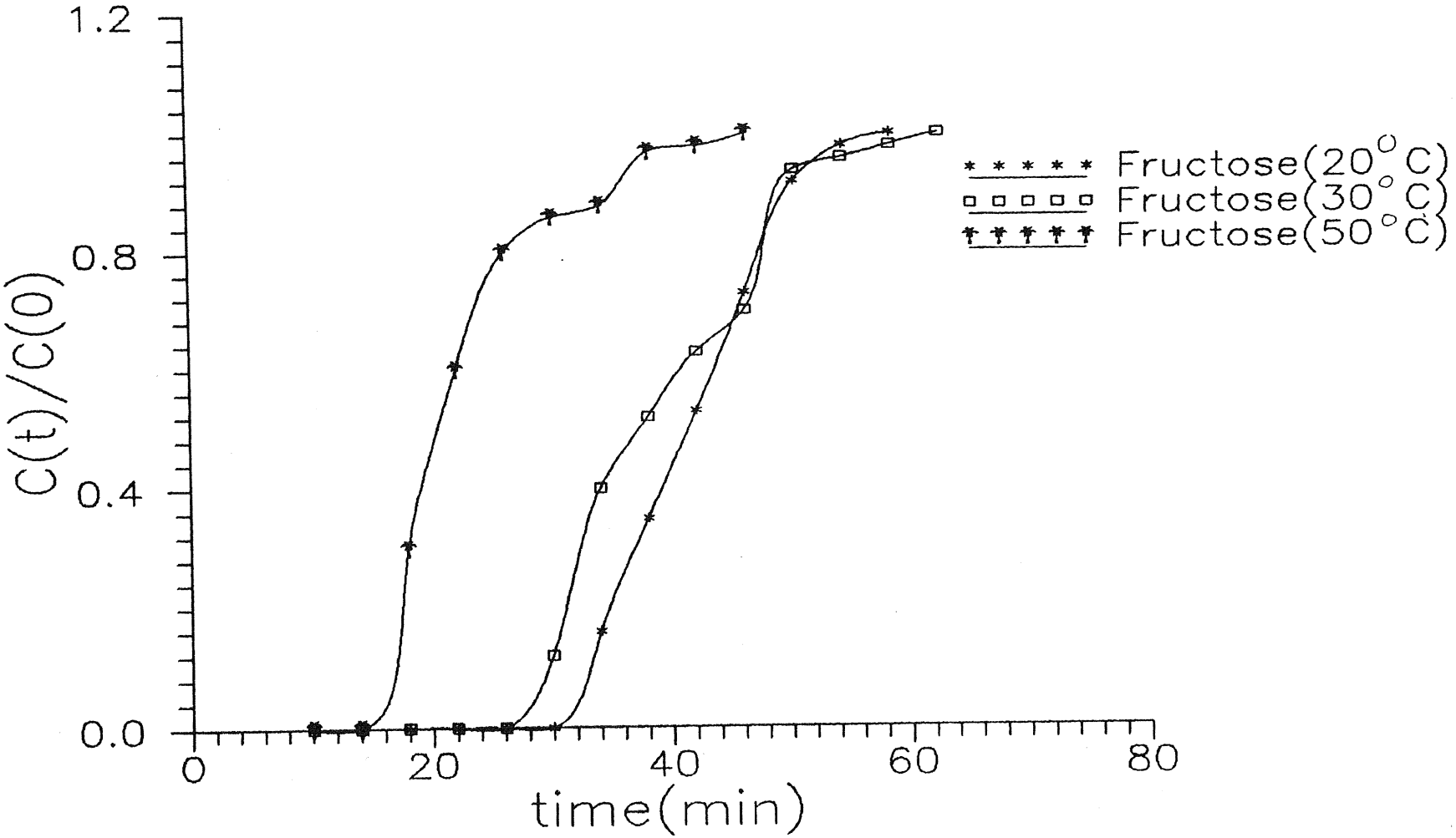


Fig. 5.10: Effect of temperature on adsorption of fructose (run 11, 12, 13)

Table 5.9 : Important parameters for the effect of concentration on adsorption of glucose and fructose :

Parameter	run 14,17	run 15,18	run 16,19
Resin	RDL-90-8	RDL-90-8	RDL-90-8
Feed concentration(mol/lit.)	0.05	0.20	0.50
Temperature(^{0}C)	30	30	30
Feed flowrate (ml/min)	1.2	1.2	1.2
Bed diameter(cm)	1.5	1.5	1.5
Volume of the bed (cm^3)	94.2	94.2	94.2
Bed voidage (ϵ)	0.31	0.31	0.31

Table 5.10 : Results for the effect of concentration on adsorption of glucose and fructose :

Parameter	Glucose			Fructose		
	run 14	run 15	run 16	run 17	run 18	run 19
Breakthrough time (min)	22	18	12	30	26	20
Saturation time (min)	54	46	30	62	54	36

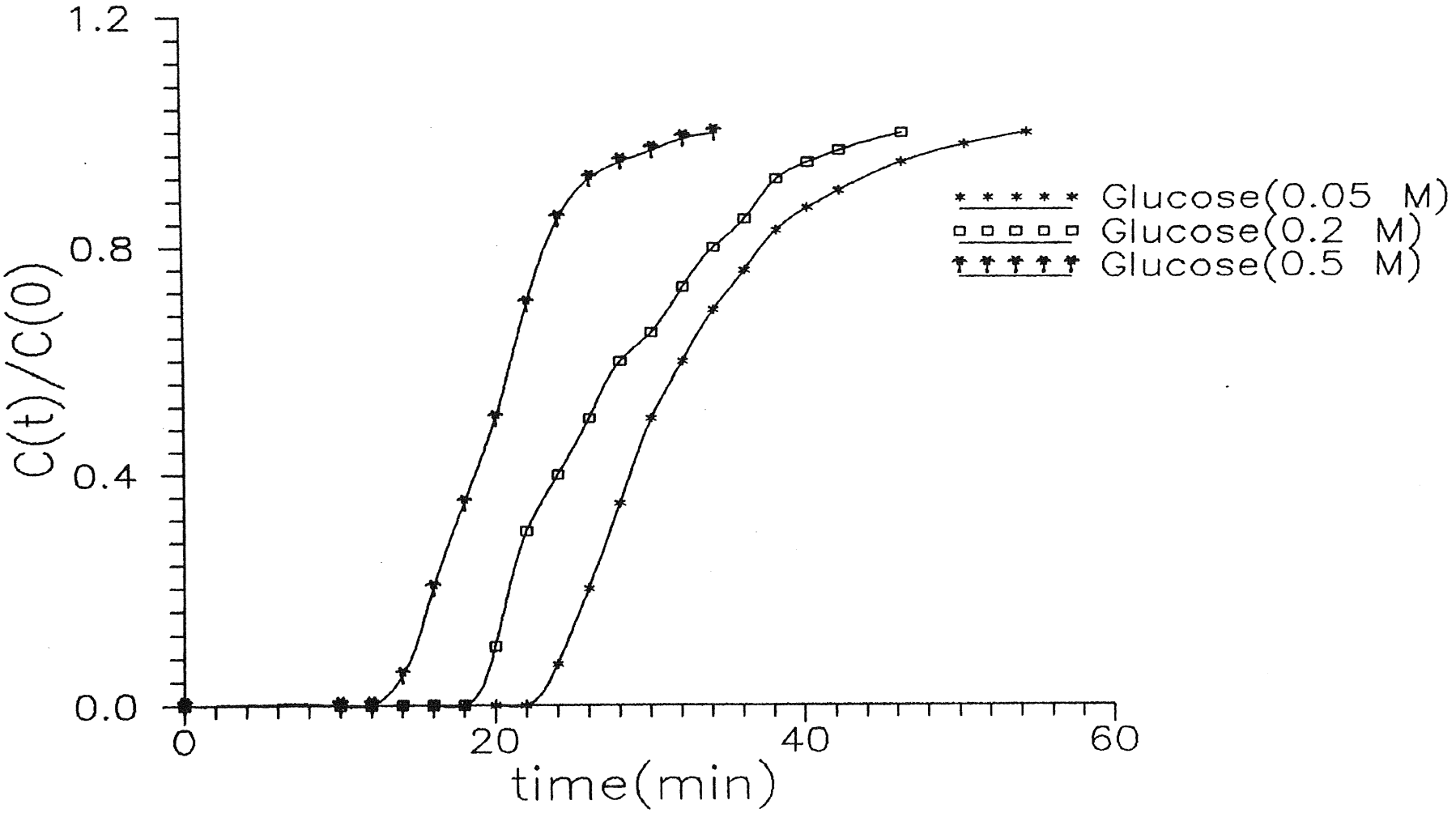


Fig. 5.11: Effect of concentration on adsorption of glucose (run 14,15,16)

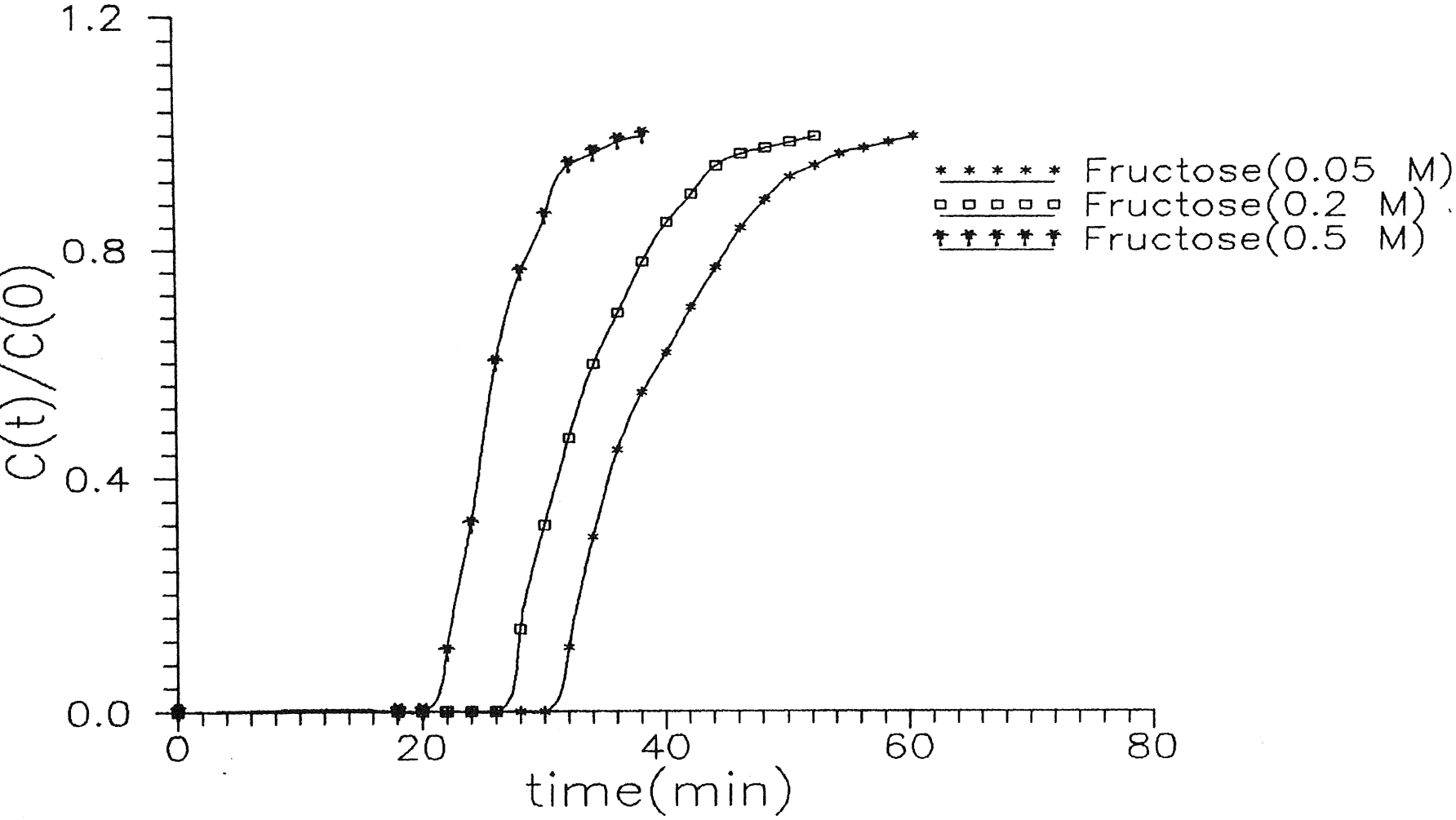


Fig. 5.12: Effect of concentration on adsorption of fructose (run 17, 18, 19)

5.2.3 Design of the simulated moving bed apparatus :

PRODASS is a software which involves the process design for an adsorption separation system. Using this software, a particular adsorption system can be simulated, designed and different parameters can be estimated. It involves the variation of different parameters like the concentration of the solute, bed height, bed porosity, flowrate of the feed, cycle time etc. Changing any of these parameters gives different values of percentage of the desired component in extract and raffinate phases. This software can used for a single component as well as for multicomponent adsorption process. For this the equilibrium constant of the individual components (glucose and fructose) was need to be calculated. The equilibrium constant was obtained with the help of breakthrough curve (saturation time).

Calculation of equilibrium constant :

For this, the data of run 10 was used.

a) Equilibrium constant of glucose :

Saturated volume = (time taken for saturation) × feed flowrate

= 54 min. × 1.2 ml/min.

= 64.8 cm^3

Moles coming out of the bed = Saturation volume × (area under the curve / total area) × C_0

= 64.8 × [116.98/ (16×18)] × 0.05

= 1.3158 gmole.

Moles remaining in the bed = Saturated volume × [1- (area under the curve / total area)] × C_0

= 64.8 × [1- {116.98/ (16×18)] × 0.05

= 1.92396 gmole.

Saturated concentration(q_0) = Moles remaining / total volume of the bed

$= 1.92396 / 94. = 0.020424$ gmole / cc.

Equilibrium constant $= q_0 / [C_0 / (1 - \epsilon)]$ where ϵ = bed voidage

$= 0.020424 / [0.05(1 - 0.31)]$

$= 0.59$

Similarly, equilibrium constant of fructose was found using the same procedure. It was 0.65. It is quite evident that it is greater than glucose.

5.3 Testing of model for the Separation of glucose and fructose in simulated moving bed apparatus :

Problem :

Hashimoto et.al.(35) analyzed fractionation of glucose-fructose mixture. Their simulated moving bed adsorber consisted of 16 columns, each of 1.38×10^{-2} m diameter and 0.102 m length, which were placed on a rotating disc. Each column was connected to a valve which could be connected to next column or a bleed or a feed point. The columns were packed with Y zeolite (Ca^{+2} form). Each zone of simulated moving bed had four columns of adsorbent. The experimental parameters for run S-5 [given in table (5.11)] are used for simulation study.The authors did not report the porosity of the bed. Our fixed bed had porosity of 0.33. Hence a value 0.4 is assumed.

The simulated concentration profile along with the experimental data are shown in fig. 5.13. The figure 5.13 and table 5.12 show that the experimental profiles are in fair agreement with the profiles calculated by the two models i.e. intermittent moving bed model(unsteady state model)[Hashimoto et.al.(35)] and hypothetical moving bed model.

The calculated concentration profiles in case of hypothetical moving bed model are not in complete agreement with the experimental observation (refer fig. 4.1 for schematic representation of hypothetical moving bed adsorber). The deviation in case

Table 5.11: Experimental parameters for run 20[Hashimoto et.al.{(35) runS-5}]

Adsorbent	Y zeolite Ca^{+2} form
Feed concentration(glucose)(mol/lit.)	0.5
Feed concentration(fructose)(mol/lit.)	0.5
Column length(m)	0.102
Column diameter(m)	1.38×10^{-2}
Feed flowrate (m^3/s)	1.67
Desorbent flowrate(m^3/s)	5.00
Extract flowrate(m^3/s)	3.33
Raffinate flowrate(m^3/s)	3.33
Velocities of liquid in each zone(m/s)	
V_1	5.13
V_2	7.89
V_3	6.17
V_4	8.40
Column configuration	4 : 4 : 4 : 4
Distribution coefficient(glucose)	0.586
Distribution coefficient(fructose)	0.686
Mass tranfer coefficient(sec^{-1})	6.84×10^{-3}
Temperature(^{0} C)	50

Table 5.12 : Results for run 20 [Hashimoto {(35) run S-5}]

The concentration is expressed in mol/lit.

Position	Experimental		Intermittent moving bed model (Hashimoto)		Hypothetical moving bed model	
	Glu.	Fru.	Glu.	Fru.	Glu.	Fru.
Zone 1 exit	0.001	0.001	0.001	0.0009	0.0015	0.0076
Raffinate	0.18	0.125	0.22	0.17	0.196	0.133
Feed(up)	0.32	0.36	0.33	0.35	0.423	0.422
Feed(below)	0.31	0.33	0.30	0.32	0.387	0.388
Extract	0.065	0.11	0.055	0.10	0.059	0.123
Zone 4 entrance	0.0005	0.002	0.0005	0.002	0.0005	0.0026

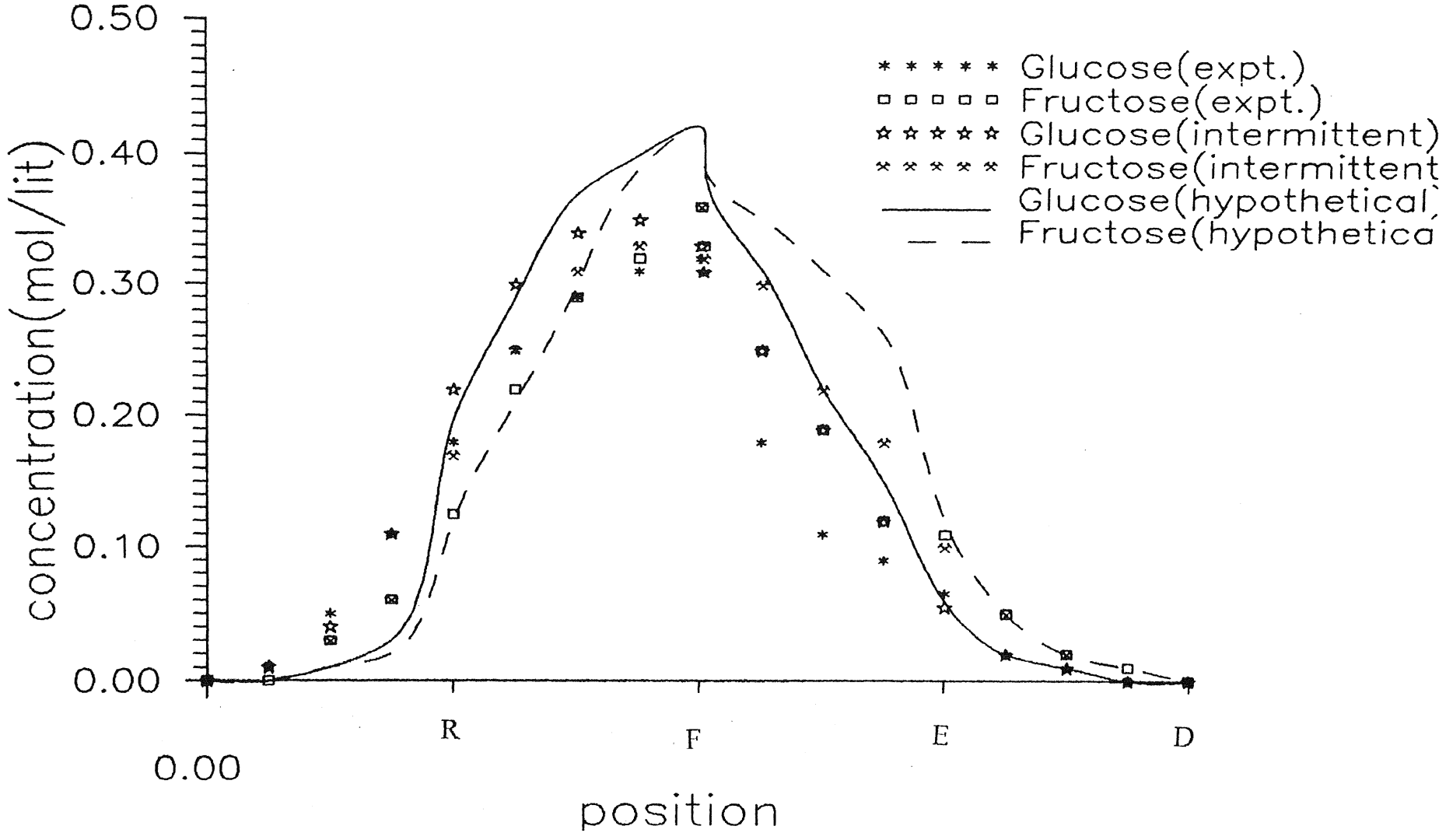


Fig. 5.13: The concentration profiles in simulated moving bed operation (run 20)

of glucose is more pronounced than fructose. The deviation may be due to exclusion of dispersion effects. Though the overall mass transfer coefficient mainly depends on the hydrodynamics of the flow, here a constant value of the mass transfer coefficient was assumed throughout the unit. The assumption of the external porosity could also give rise to the discrepancies. Nevertheless, the trend of the calculated concentration profile is similar to that of experimental data.

5.4 Effect of operating parameters for an effective performance in simulated moving bed operation :

The operating parameters such as switch time, column length, flowrates of extract, raffinate, feed, desorbent were varied to check for better separation. Also, according to product specification the parameters could be chosen. The hypothetical moving bed model provides an easier way to check the effect of parameters.

The definitions of the terms used in the analysis of the performance of simulated moving bed apparatus like fructose purity (F.P.), glucose purity (G.P.), fructose recovery in extract w.r.t. feed (F.R.), glucose recovery in raffinate w.r.t. feed (G.R.), extract molar rate are similar to those in fixed bed operation.

For the effect of parameters the same experimental parameters of Hashimoto et.al.(35) (run S-5) were used.

The parameter β_{nK} which is already defined in modeling plays an important role in determining operating conditions. The criterion of β_{nK} has to be met for attaining a good separation of glucose and fructose.

The physical meaning of β_{nK}[35] can be given as follows :

$$\beta_{nK} = \frac{u_n}{u_s(1-\epsilon)\, m_K}$$

$$= \frac{\text{amount of adsorbate transported by fluid phase}}{\text{amount of adsorbate transported by solid phase}}$$

Thus, when β_{nK} is less than unity, the amount of adsorbate carried by the adsorbent is more than that carried by the liquid. Hence, the range of β_{nK} values allowable to obtain good separation must be set in the mode as shown below.

Zone n	1	2	3	4
β_{nG}	<1	>1	>1	>1
β_{nF}	<1	<1	<1	>1

5.4.1 The effect of switch time :

Keeping other parameters constant, the switch time was varied as shown in table 5.13. Results with original switch time (120 sec.) are shown in bold font. As shown in table 5.13, as the switch time is decreased, the fructose purity decreases, but glucose purity increases. But fructose recovery and extract molar rate first increases then falls at 112 seconds. This may be due to enough fructose molecules are not able to reach extract zone.

Hence, for H.F.S. requirement of 60 % purity switch time of 114 seconds is recommended.

If switch time is increased, the fructose increases upto 136 seconds and then decreases, but glucose purity increases continuously. Fructose recovery and extract molar rate falls drastically. For 70 % H.F.S. purity, switch time of 124 seconds is recommended.

As shown in table 5.14, for switch time of 120 seconds, all β values except β_{F2} and β_{G3} agree with the criterion for good separation. But still β_{G2} is greater than β_{F2}. It means for glucose it is more pull towards raffinate phase than fructose. The same

Table 5.13 : Effect of switch time on separation parameters

Time (sec.)	F.P. (%)	G.P. (%)	F.R. (%)	G.R. (%)	E.M.R. ($\times 10^2$) (mol/min)
112	53.82	61.12	51.32	24.92	2.865
114	60.32	61.64	58.43	28.64	2.91
116	63.14	61.12	57.05	32.32	2.72
118	65.23	60.42	53.12	35.96	2.41
120	**67.45**	**59.65**	**48.94**	**39.32**	**2.17**
122	69.54	58.66	44.43	42.46	1.91
124	71.56	57.64	39.72	45.21	1.66
126	73.33	56.67	35.03	47.77	1.44
128	74.96	55.63	28.41	46.42	1.14
130	76.12	54.83	26.39	51.78	1.03
132	76.91	53.92	20.22	48.12	0.79
134	77.13	53.35	19.04	54.75	0.74
136	76.44	52.67	16.02	55.89	0.63
138	75.70	52.31	14.71	56.32	0.58

Table 5.14 : Effect of switch time on β values

Time	β_{F1}	β_{G1}	β_{F2}	β_{G2}	β_{F3}	β_{G3}	β_{F4}	β_{G4}
112	0.39	0.47	0.99	1.16	0.69	0.81	1.29	1.50
114	0.42	0.49	1.02	1.20	0.72	0.85	1.33	1.55
116	0.45	0.52	1.06	1.24	0.75	0.88	1.37	1.60
118	0.47	0.55	1.09	1.28	0.78	0.91	1.40	1.65
120	**0.49**	**0.58**	**1.13**	**1.32**	**0.81**	**0.95**	**1.44**	**1.69**
122	0.52	0.60	1.16	1.36	0.84	0.98	1.49	1.74
124	0.54	0.64	1.20	1.4	0.87	1.02	1.53	1.79
126	0.57	0.67	1.23	1.45	0.90	1.05	1.57	1.84
128	0.59	0.69	1.27	1.49	0.93	1.09	1.61	1.88
130	0.61	0.72	1.30	1.53	0.96	1.12	1.65	1.93
132	0.64	0.75	1.34	1.57	0.99	1.16	1.69	1.98
134	0.67	0.78	1.37	1.61	1.02	1.19	1.73	2.02
136	0.69	0.81	1.41	1.65	1.05	1.23	1.77	2.07
138	0.7	0.82	1.43	1.67	1.06	1.24	1.79	2.09

reason applies to β_{G3}. Hence, overall it is a good separation.

For switch time of 138 seconds, β_{F2} far exceeds 1. Also β_{F3} doesn't agree with the criterion. Hence it proves to a bad separation.

5.4.2 The effect of column length :

Keeping other parameters constant, the column length was varied as shown in table 5.15. Results with original length (0.102 m) are shown in bold font.

As shown in table 5.15, as length decreases, the fructose purity first increases upto 9.2 cm length and then falls. But glucose purity continuously decreases. Fructose recovery and extract molar rate continuously decreases. Hence, for 75 % fructose purity requirement column length of 9.2 cm is recommended.

When length is increased, fructose purity decreases slowly but drastically becomes low at 11 cm length. The same applies to fructose recovery. The extract molar rate first increases then decreases at 11 cm length.

Thus for 60 % fructose purity length of 10.9 cm is recommended.

As shown in table 5.16, the β values for 0.102 m length are in bold font. Here again at length < 9.0, $\beta_{F2} > 1.4$ and also $\beta_{F3} > 1$. Hence it shows a bad separation.

5.4.3 The effects of flowrates of extract and raffinate :

Keeping other parameters constant, the extract, raffinate flowrates were varied as shown in table 5.17. The fructose purity falls slowly upto extract flowrate of 4.53×10^{-8} m^3/s but falls drastically at 4.73×10^{-8} m^3/s. The glucose purity increases steadily but falls at extract flowrate of 4.73×10^{-8} m^3/s. Fructose recovery and extract molar rate increases steadily but drastically fall at extract flowrate of 4.73×10^{-8} m^3/s.

When extract flowrate is decreased, fructose purity increases steadily but never falls unlike effect of switch time and column length. Glucose purity also continuously decreases. Fructose recovery and extract molar rate drastically falls.

Table 5.15: Effect of column length on separation parameters

Length (cm)	F.P.(%)	G.P.(%)	F.R.(%)	G.R.(%)	E.M.R. ($\times 10^{-2}$) (mol/min)
8.6	64.90	51.25	12.21	57.42	0.565
8.8	70.15	51.92	14.51	56.42	0.622
9.0	73.37	52.70	17.69	55.10	0.720
9.2	74.65	53.60	21.70	53.40	0.870
9.4	74.49	54.63	26.44	51.39	1.060
9.6	73.39	55.79	31.78	48.95	1.300
9.8	71.70	57.03	37.49	46.12	1.570
10.0	69.66	58.33	43.29	42.88	1.860
10.2	**67.40**	**59.61**	**48.87**	**39.28**	**2.170**
10.4	64.87	60.78	53.59	35.39	2.480
10.6	62.25	61.75	57.28	31.32	2.760
10.8	59.98	62.44	60.74	27.22	3.040
10.9	58.83	61.51	62.12	25.20	3.170
11.0	45.14	62.89	47.32	23.23	2.360

Table 5.16 : Effect of column length on β values

Length	β_{F1}	β_{G1}	β_{F2}	β_{G2}	β_{F3}	β_{G3}	β_{F4}	β_{G4}
8.6	0.77	0.90	1.52	1.78	1.14	1.34	1.90	2.22
8.8	0.72	0.85	1.46	1.71	1.09	1.28	1.83	2.15
9.0	0.69	0.81	1.41	1.65	1.05	1.23	1.77	2.07
9.2	0.66	0.77	1.36	1.59	1.00	1.17	1.71	2.00
9.4	0.62	0.72	1.31	1.53	0.96	1.13	1.65	1.94
9.6	0.58	0.69	1.26	1.48	0.92	1.08	1.60	1.87
9.8	0.55	0.65	1.21	1.42	0.88	1.03	1.54	1.81
10.0	0.52	0.61	1.17	1.37	0.85	0.99	1.49	1.75
10.2	**0.49**	**0.58**	**1.13**	**1.32**	**0.81**	**0.95**	**1.44**	**1.69**
10.4	0.47	0.55	1.09	1.27	0.78	0.91	1.40	1.64
10.6	0.44	0.51	1.05	1.23	0.74	0.87	1.35	1.59
10.8	0.41	0.48	1.01	1.18	0.71	0.84	1.31	1.54
10.9	0.40	0.47	0.99	1.16	0.69	0.81	1.29	1.51
11.0	0.38	0.46	0.98	1.14	0.68	0.80	1.27	1.49

Table 5.17:Effect of extract and raffinate flowrates on separation parameters

E ($\times 10^8$) (m^3/s)	R ($\times 10^8$) (m^3/s)	F.P.(%)	G.P.(%)	F.R.(%)	G.R (%)	E.M.R. ($\times 10^2$) (mol/min)
3.33	**3.33**	**67.40**	**59.61**	**48.87**	**39.28**	**2.17**
3.43	3.23	66.20	60.32	51.34	37.94	2.33
3.53	3.13	65.00	61.00	53.58	36.46	2.47
3.63	3.03	63.76	61.72	59.77	36.26	2.81
3.73	2.93	62.57	62.41	63.33	35.82	3.04
3.83	2.83	61.34	63.07	66.62	35.42	3.26
3.93	2.73	60.34	63.71	70.32	34.11	3.5
4.03	2.63	59.27	64.32	73.54	32.66	3.72
4.13	2.53	58.24	64.92	76.58	31.07	3.95
4.33	2.33	56.90	65.90	83.82	27.56	4.4
4.53	2.13	54.26	67.20	85.15	23.74	4.7
4.73	1.93	27.52	63.51	30.06	19.80	3.28
3.13	3.53	69.75	58.20	41.75	39.60	1.80
2.93	3.73	71.97	56.86	34.98	39.54	1.460
2.73	3.93	73.86	55.63	28.79	39.00	1.170
2.53	4.13	75.55	54.55	23.30	38.18	0.927
2.33	4.33	77	53.62	18.67	37.19	0.725
2.13	4.53	78.22	52.84	14.58	36.09	0.560
1.93	4.73	79.24	52.19	11.30	34.95	0.420
1.53	5.13	80.77	51.26	6.51	32.69	0.242
1.13	5.53	81.82	50.68	3.50	30.56	0.128

Table 5.18 : Effect of extract and raffinate flowrates on β values

Ext.	Raf.	β_{F1}	β_{G1}	β_{F2}	β_{G2}	β_{F3}	β_{G3}	β_{F4}	β_{G4}
3.33	**3.33**	**0.49**	**0.58**	**1.13**	**1.32**	**0.87**	**0.95**	**1.45**	**1.69**
3.43	3.23	0.49	0.58	1.11	1.3	0.79	0.93	1.45	1.69
3.53	3.13	0.49	0.58	1.09	1.28	0.77	0.90	1.45	1.69
3.63	3.03	0.49	0.58	1.07	1.25	0.75	0.89	1.45	1.69
3.73	2.93	0.49	0.58	1.05	1.236	0.73	0.86	1.45	1.69
3.83	2.83	0.49	0.58	1.04	1.21	0.71	0.84	1.45	1.69
3.93	2.73	0.49	0.58	1.01	1.19	0.69	0.81	1.45	1.69
4.03	2.63	0.49	0.58	0.99	1.16	0.67	0.79	1.45	1.69
4.13	2.53	0.49	0.58	0.97	1.14	0.66	0.77	1.45	1.69
4.33	2.33	0.49	0.58	0.94	1.10	0.62	0.72	1.45	1.69
4.53	2.13	0.49	0.58	0.90	1.05	0.58	0.68	1.45	1.69
4.73	1.93	0.49	0.58	0.86	1.01	0.54	0.64	1.45	1.69
3.13	3.53	0.49	0.58	1.17	1.370	0.85	0.99	1.45	1.69
2.93	3.73	0.49	0.58	1.2	1.41	0.89	1.04	1.45	1.69
2.73	3.93	0.49	0.58	1.25	1.46	0.93	1.08	1.45	1.69
2.53	4.13	0.49	0.58	1.28	1.50	0.96	1.13	1.45	1.69
2.33	4.33	0.49	0.58	1.32	1.55	1.0	1.17	1.45	1.69
2.13	4.53	0.49	0.58	1.36	1.59	1.04	1.22	1.45	1.69
1.93	4.73	0.49	0.58	1.40	1.64	1.08	1.26	1.45	1.69
1.53	5.13	0.49	0.58	1.47	1.73	1.15	1.35	1.45	1.69
1.13	5.53	0.49	0.58	1.55	1.81`	1.23	1.44	1.45	1.69

Hence, for 75 % fructose purity extract flowrate of 2.53×10^{-8} m^3/s is recommended. For 60 % fructose purity extract flowrate of 3.93×10^{-8} m^3/s is recommended.

The effect of variation of extract, raffinate flowrate on β values is shown in table 5.18. The parameters $\beta_{F1}, \beta_{G1}, \beta_{F4}, \beta_{G4}$ remain constant throughout. The other four β values are controlling the separation.

5.4.4 The effects of flowrates of feed and desorbent :

Keeping other parameters constant, the feed and desorbent flowrates were varied as shown in table 5.19.

As feed flowrate is decreased and desorbent flowrate increased the fructose purity and recovery both increases, but extract molar rate decreases as it is evident. Hence, for 75 % fructose purity feed flowrate of 0.97×10^{-8} m^3/s is recommended.

As feed flowrate is increased, the fructose purity and recovery decreases steadily but extract molar rate increases. For 60 % fructose purity, feed flowrate of 2.37×10^{-8} m^3/s is recommended.

The effect of variation of feed, desorbent flowrates on β values is shown in table 5.20. Here parameters β_{F1}, β_{G1}, β_{F2}, β_{G2} remain constant throughout.

Thus, effect of variation of operating parameters provide an effective method to determine optimal separation. The β values can be chosen according to product specification. As discussed elsewhere the design of a simulated moving bed adsorber is an important task for economical production of High fructose syrups. In practice a simulated moving bed design is about 3 - 4 times more effective than the fixed bed adsorber. The fructose content in the extract (H.F.S.) could be increased to a level of about 75 % starting with a feed composition of 50 : 50 glucose and fructose. The desired composition for the commercial syrups is about 55 % fructose content in

Table 5.19 : Effect of feed and desorbent flowrates on separation parameters

F($\times 10^8$) (m^3/s)	D($\times 10^8$) (m^3/s)	F.P.(%)	G.P.(%)	F.R.(%)	G.R.(%)	E.M.R. ($\times 10^2$) (mol/min)
1.67	**5.0**	**67.4**	**59.61**	**48.87**	**39.28**	**2.17**
1.57	5.1	68.45	59.42	50.2	40.23	2.07
1.47	5.2	69.48	59.19	51.6	41.13	1.96
1.37	5.3	70.5	58.93	53.2	41.98	1.86
1.17	5.5	72.46	58.33	57.08	43.52	1.66
0.97	5.7	74.28	57.65	62.49	44.83	1.49
0.67	6.0	76.67	56.57	77.12	46.42	1.21
1.77	4.9	66.36	59.75	47.66	38.3	2.28
1.97	4.7	64.34	59.91	45.43	36.3	2.5
2.17	4.5	62.38	59.87	43.26	34.14	2.7
2.37	4.3	60.81	59.7	41.58	32.07	2.9
2.57	4.1	58.63	59.33	38.6	30.11	3.04
2.77	3.9	57.3	58.67	36.78	28.31	3.2

Table 5.20 : Effect of feed and desorbent flowrates on β values

Feed	desor.	β_{F1}	β_{G1}	β_{F2}	β_{G2}	β_{F3}	β_{G3}	β_{F4}	β_{G4}
1.67	**5.0**	**0.49**	**0.58**	**1.13**	**1.32**	**0.81**	**0.95**	**1.45**	**1.69**
1.57	5.1	0.49	0.58	1.13	1.32	0.83	0.97	1.47	1.72
1.47	5.2	0.49	0.58	1.13	1.32	0.85	0.99	1.48	1.74
1.37	5.3	0.49	0.58	1.13	1.32	0.87	1.01	1.50	1.76
1.17	5.5	0.49	0.58	1.13	1.32	0.90	1.06	1.55	1.80
0.97	5.7	0.49	0.58	1.13	1.32	0.95	1.10	1.58	1.85
0.67	6.0	0.49	0.58	1.13	1.32	1.0	1.18	1.64	1.92
1.77	4.9	0.49	0.58	1.13	1.32	0.79	0.93	1.43	1.67
1.97	4.7	0.49	0.58	1.13	1.32	0.76	0.88	1.39	1.63
2.17	4.5	0.49	0.58	1.13	1.32	0.71	0.84	1.35	1.58
2.37	4.3	0.49	0.58	1.13	1.32	0.68	0.79	1.32	1.54
2.57	4.1	0.49	0.58	1.13	1.32	0.64	0.75	1.28	1.49
2.77	3.9	0.49	0.58	1.13	1.32	0.60	0.70	1.24	1.45

H.F.S. Fig. 5.14 shows a schematic process flow diagram for an industrial process for the production of fructose and High fructose syrups from two different routes.

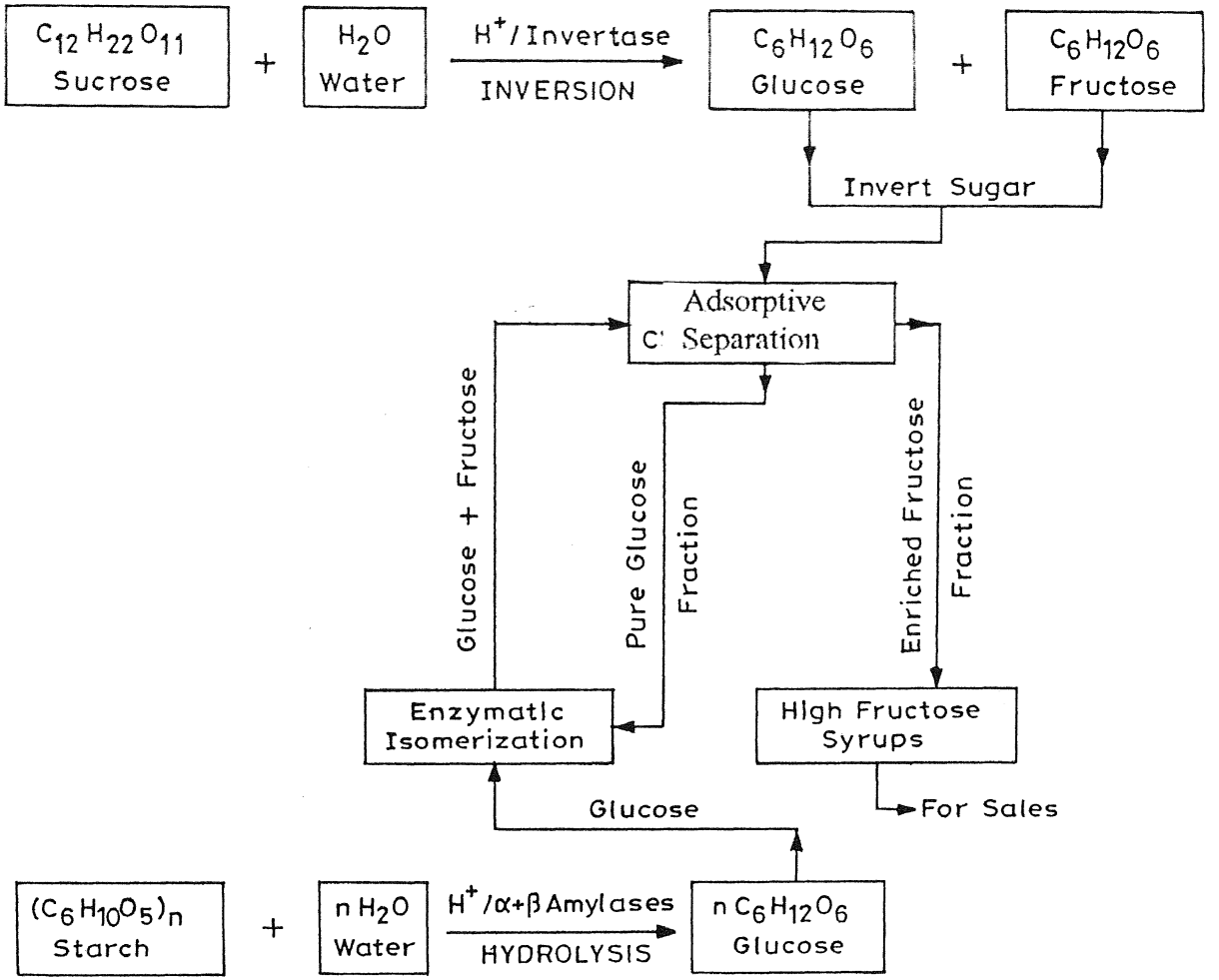


Fig. 5.14: The methods of production of fructose and High fructose syrups

Chapter 6

Conclusions and Scope for future work

Conclusions :

Fructose may be obtained as a mixture with glucose from two alternative sources viz. a) an isomerization of glucose and b) on inversion of sucrose in nearly equimolar compositions. Enrichment of fructose from such mixtures produces high fructose syrups. The indigenous resins have been successfully tested for the separation of glucose and fructose from their aqueous mixtures in fixed bed adsorber. The effects of flowrate, feed concentration and bed height were studied. All the three parameters are found to be important to obtain optimum results. The breakthrough curves of glucose and fructose were determined. The effects of feed concentration and temperature on breakthrough curves were studied. The saturation time was found to be a strong function of these parameters. The equilibrium constants could be calculated from the breakthrough curves. The adsorbents used in this study are found to be very effective for the separation of glucose and fructose.

A mathematical model for the simulated moving bed adsorber has been proposed assuming that the external mass transfer resistance is a controlling step. The equations were put in matrix form and solved using the Gauss-Jordan technique. The concentration profiles were compared with the experimental data. A good agreement between experimental and predicted values was obtained. Some deviations noted may be attributed to the internal resistance within the particle and to axial dispersion effects.

The effects of switch time, length of the column and the flowrates of extract,

raffinate, feed and desorbent flowrates on the product composition have been studied. The operating parameters may be manipulated to obtain the optimum results. Fructose content of about 70 percent in the extract stream (H.F.S.) could be obtained by manipulating the operating parameters in simulated moving bed operation.

Scope for future work :

There is a need to look into some other important and interesting aspects of the fixed bed and simulated moving bed process. The possible areas of future investigation are as follows.

1) In this study, fructose-glucose system has been considered. Other binary systems may be used to test the proposed model in both fixed bed and simulated moving bed operations under varying operating conditions.

2) Studies may be undertaken involving recycling of eluent streams to test the performance of fixed bed operations.

4) The present model is based on the linear uncoupled adsorption isotherms. This may be extended for the cases of non linear coupled isothermal and nonisothermal operations.

References

1) Gehlawat J.K., " High fructose syrup as a substitute for sugar ", J. Sci. Ind. Res., 50, 989 (1991)

2) Gehlawat S. and Gehlawat J.K., " Cheaper High fructose Syrups from Cane-juice-Also Effective sugar output up by 20 percent "Chem. Ind. News, 40, 595 (1995)

3) Kumar S. and Gehlawat J.K.,"Sugarcane- A cost effective source of high fructose syrup", J Sci. Ind. Res., in press, 1996

4) Schoenrock Karlheinz W.R., Kearney Michael M., Rearick, Engene D., " Sorption and separation of dissolved constituents ", US Pat. Appl 267,065,26 May, 1981, p.33, Chem. Abstracts, 98 (1983) 91351c

5) Doelle M.B. and Doelle H.W., Biotechnol. Lett., 13, 875 (1991)

6) Monsoon P. and Combes D., " Application of immolized invertase to continuous hydrolysis of concentrated sucrose solutions ",Biotechnol. Bioengg., 26,347 (1984)

7) Mansfield J., Schellenberger A. and Rombach J., " Application of polystyrene based invertase to continuous sucrose hydrolysis on pilot scale ", Biotechnol. Bioeng.,40,997(1992)

8) Anon, " A Biotech. Process for Invert Sugar,"Business Line, 126 (2 June 1993)

9) Levesque C.L. and Craig A.M., " Kinetics of an esterification with cation exchange resin catalyst ",Ind. Eng. Chem., 40, 96 (1948)

10) Fodor J. and Hajos Z., Acta Chim Acad. Sci. Hung., 7, 133 (1955)

11) Kulhaneck Milos and Tadra Milan, Czech CS 206, 710, 15 Sept. Chem. Abstr., 100 (1984)105451j

12) Anon, " Breakthrough in demineralising sugarcane juice" Chem, Week, (13 April 1993),p.114

13) Kumar R., Singh V., Rastogi S., Brar P., Mehta R.N. and Raina P., Proc 54th STAI Convent (1992) p.1

14) Sharma M.V.J., Malshe V.C. and Gehlawat J.K., " Studies in ultrafiltration of sugarcane juice " Proc CHEMCON-93, Bombay, (December 1993) p.1

15) Gehlawat J.K., Proc STAI Seminar, Bhubaneshwar, (April 1995) p.29

16) Sinha C. and Gehlawat J.K., " Inversion of sucrose with cation resins ", Indian J Chem. Technol., 2 (1995) p. 171

17) Thomas B.P. and Logan R.M., " Continuous crystallization of fructose " , U.S. Patent 4,895,601, Dec. 1989, Chem. Abstr. 112, 201003h, 1990.

18) Niekamp C.W. and Seidman M., " Enrichment of fructose syrups ", US Patent 4,888,060. Dec. 1989, Chem. Abstr. 112, 201004j, 1990.

19) Shiau L.D., "Crystallization of fructose from aqueous solutions", Ph.D. Dissertation, Michigan state university (1998)

20) Niranjan T., " Studies on the separation of glucose and fructose from their aqueous mixtures", M.Tech. thesis, I.I.T. Kanpur (1990).

21) Broughten D.B., "Molex : Case history of a process", Chem.Eng.Prog., 64(8), 60-65 (1968)

22) Howard A.J., Carta G. and Byers C.H., "Separation of sugars by continuous annular chromatography", Ind. Eng. Chem. Res., 27, 1873-1882 (1988)

23) Rhee H.K., Aris R. and Amundson N.R., "First order partial differential equations : Volume 1(Theory and applications of single equations), Prentice Hall, Englewood Cliffs, NJ, (1986)

24) Rhee H.K., Aris R. and Amundson N.R., "First order partial differential equations : Volume 2(Theory and applications of Hyperbolic systems of quasilinear equations), Prentice Hall , Englewwod Cliffs, NJ, (1989)

25) Rodrigues A.E. and Daniel Tondeur, " Percolation processes : Theory and

applications", NATO ASI Series No. 33, Sijthoff and Noordoff , The Netherlands(1981)

26) Ruthven D.M., "Principles of adsorption and adsorption processes", John Wiley, New York(1984)

27) Thomas H.C., "Chromatography : A problem in Kinetics", Ann. NY. Acad. Sci. , 49,161-182(1948)

28) Rosen J.B., "General numerical solutions for solid diffusion in fixed beds", Ind. Eng. Chem., 46(8), 1590-94(1954)

29) Kasten P.R. and Amundson N.R., "Analytical solution for simple systems in moving bed adsorbers", Ind. Eng. Chem., 44(7), 1704(1952)

30) Yoon S.M. and Kunii D., "Physical adsorption in a moving bed of fine adsorbents", Ind. Eng. Chem., 10(1), 64(1971)

31) Ching C.B., " A theoretical model for the simulation of the operation of the Semicontinuous Chromatographic refiner for separating glucose and fructose", J. Chem. Eng. Jap., 16(1),49(1983)

32) Ching C.B. and Ruthven D.M., " An experimental study of a Simulated countercurrent adsorption system 1: Isothermal steady state operation", Chem. eng. Sci., 40, 877(1985a)

33) Ching C.B. and Ruthven D.M., " An experimental study of a Simulated countercurrent adsorption system 2: Transient response", Chem. Eng. Sci., 40, 887(1985b)

34) Lee K.N. and W.K. Lee, " A theoretical model for the separation of glucose and fructose mixtures by using a semicontinuous chromatographic refiner", Separation Sci. and Tech., 27, 295(1982)

35) Hashimoto K., S.Adachi, H. Noujima and H. Maruyama, " Models for the separation of Glucose-Fructose mixture using a simulated moving bed adsorber",

J. Chem. Eng. Jap., **16**, 400(1983)

36) Hidajat K., C.B.Ching and D.M. Ruthven," Numerical simulation of a semicontinuous countercurrent adsorption unit for fructose-glucose separation", Chem. Eng. J., **33**, B55(1986a)

37) Ching C.B., Chu K.H., K. Hidajat and M.S. Uddin, "Experimental and modeling studies on the transient behaviour of a Simulated Countercurrent adsorber", J. Chem. Eng. Jap., **24**, 614(1991)

38) Ching C.B. and Ruthven D.M., "Experimental study of a Simulated Countercurrent adsorption system 4: Non-isothermal operation", Chem. Eng. Sci., **41**, 3603(1986a).

39) Ching C.B. and D.M. Ruthven, "An improved adsorption process for the production of High-fructose syrup", AICHE J., **32**, 1876(1986b).

40) Hashimoto K., M. Yamada, S.Adachi and Y. Shirai, " A Simulated moving bed adsorber with three zones for continuous separation of Lphenylalanine and NaCl", J. Chem. Eng. Jap., **22**,432(1989)

41) Fish B.B., Carr R.W. and Aris R., " The continuous countercurrent moving bed separator",AICHE J. 35(5), 737-745(1989)

42) Ching C.B., K.H.Chu, K. Hidajat, Uddin M.S., "Comparative study of flow-schemes for a simulated countercurrent adsorption separation process",AICHE J., 38 (11), 1744(November 1992)

43) Sarmidi M.R., Barker P.E., "Simultaneous biochemical reaction and separation in a rotating annular chromatograph", Chem.Eng. Sci., **48**(14), 2615-23(1993).

44) Prasad A.," Simulation of simulated moving bed adsorber with reference to fractionation of glucose-fructose mixture", M.Tech. thesis, I.I.T. Kanpur (1993)

45) Ching C.B. and Ruthven D.M., "Countercurrent and simulated countercurrent adsorption separation processes", Chem. Eng. Sci., **44**(5), 1011-1089(1989)

46) Shyam Sunder M. and Gehlawat J,K.," Studies on adsorption-desorption phenomena consequent to separation of glucose and fructose from their aqueous mixtures using ion-exchange resins" , I.I.T./ K, unpublished work.

Nomenclature

A	Cross sectional area of the bed of an adsorption column (m^2)
a_v	Specific surface area (m^2/m^3 of the bed)
C_0	Initial concentration of the feed (mol/lit.)
C_K	Concentration of the component in the mobile phase (mol/lit.)
C_K^*	Concentration of the component in the stationery phase (mol/lit.)
C_{K^*}	$C_K - C_K^*$
D	Desorbent flowrate (m^3/s)
E	Extract flowrate (m^3/s)
F	Feed flowrate (m^3/s)
K_f	Overall mass transfer coefficient (m/s)
L_A	Length of each column (m.)
m_K	Distribution coefficient of component K.
N_n	Number of columns in zone n
q_0	Saturated concentration (mol/lit.)
R	Raffinate flowrate (m^3/s)
T	Switch time (sec.)
u_S	Hypothetical velocity of the adsorbent (m/s)
u_n	Superficial velocity of the liquid flow (m/s)
V_n	Superficial velocity in the fixed bed (m/s)
z	Axial distance (m.)

Greek Letters :

ϵ	Bed voidage
β_{nK}	$u_n / \{(1-\epsilon)m_K u_S\}$
λ	$C^*_{Kno} - \beta_{nK} C_{Kno}$
α_n	$K_f a_v L_A / u_n$

Subscripts :

f	Fructose
g	Glucose
K	Component
n	zone
s	Solid phase